

IN THE UNITED STATES DISTRICT COURT
FOR THE DISTRICT OF DELAWARE

CIBA SPECIALTY CHEMICALS)	
CORPORATION, a Delaware Corporation,)	
)	C.A. No.
Cross-Plaintiff)	
)	
)	
v.)	
)	
)	
3V, INC., a Delaware Corporation,)	
)	
Cross-Defendant)	
_____)	

CROSS-COMPLAINT

Jurisdiction and Venue

1. This cross-suit arises under the patent laws of the United States, 35 United States Code, and seeks review to remedy a final decision dated July 27, 2006, of the Board of Patent Appeals and Interferences of the United States Patent and Trademark Office ("Board") in patent interference proceeding No. 105,262. This decision was partially adverse to cross-plaintiff CIBA Specialty Chemicals Corporation, holding that cross-plaintiff's claims 16-27 were not entitled to the benefit of priority based upon European priority application EP 95810042.2.

2. Review by this Court is specifically provided under 35 U.S.C. § 146 and 37 C.F.R. § 1.304. Jurisdiction of this action lies with this court under 28 U.S.C § 1331 and 28 U.S.C. § 1338(a).

3. This matter is timely brought in view of the decision of the Board entered on July 27, 2006 and the Complaint served by cross-defendant. No appeal has been taken to the United States Court of Appeals for the Federal Circuit. Venue is proper in this district pursuant to § 1391 (b) and (c).

The Parties

4. Cross-Plaintiff CIBA Specialty Chemicals Corporation ("CIBA") is a corporation of the State of Delaware having a principal place of business located at 540 White Plains Road, Tarrytown, New York.

5. Upon information and belief, Defendant 3V, Inc., ("3V") is a Delaware corporation having a principal place of business at 899 Woodstock Street, Georgetown, South Carolina.

6. Upon information and belief 3V, is the assignee of all right, title and interest in U.S. Patent 5,658,973 (the '973 patent), involved in the aforesaid interference. The '973 Patent names Giuseppe Raspanti of Bergamo, Italy, as inventor.

7. CIBA is the assignee of all right, title and interest to the invention relating to a "Synergistic Stabilizer Mixture" which is disclosed and claimed in U.S. Patent Application Serial No. 10/081,291, filed February 22, 2002 (the '291 application), which was accorded benefit of U.S. Application Serial No. 09/275,859, filed March 24, 1999; U.S. Application Serial No. 08/858,191, filed April 21, 1997; U.S. Application Serial No. 08/588,164, filed January 18, 1996; and, European Application No. 95810042.2 filed January 23, 1995. The '291 application names Francois Gugumus as inventor.

8. On May 24, 2005, the Board originally declared Interference No. 105,262 between Giuseppe Raspanti the named inventor of the '973 Patent, involved in the interference and Francois Gugumus the named inventor of U.S. Patent Application Serial No. 10/081,291.

9. Upon information and belief 3V, has all right, title and interest in the '973 Patent, which issued on August 19, 1997; and, is a real party in interest in the interference as shown by

papers filed by counsel for 3V in the interference. A copy of the '973 Patent is attached hereto as Exhibit 1.

10. CIBA has all right, title and interest in the '291 application filed on February 22, 2002, and is a real party in interest. A copy of the '291 application is attached hereto as Exhibit 2.

11. Count I of the interference reads as follows:

Count I: A COMPOSITION according to claim 1 of Raspanti (5,658,973) comprising a compound a) and compound b) in a weight ratio of 1:1, wherein:

a) is a compound of formula (X) of claim 4 of Raspanti where:

r is 2 or 3,

R in formula (III) is hydrogen and

p is 2 to 20

and

b) is a compound of formula (V) of claim 4 of Raspanti where:

R is hydrogen or methyl,

n is 1 to 10 and

p is 2 to 50

or

a method for stabilizing synthetic polymers comprising the step of adding to a polyolefin in an effective stabilizing amount of the COMPOSITION,

or

a stabilized polymer comprising a polyolefin and the COMPOSITION.

12. On July 27, 2006, the Board entered a final decision. In its final decision, the Board, erroneously, and contrary to law, granted Raspanti's (3V's) Substantive Motion 4 (Paper No. 35) for judgment that Gugumus (CIBA) claims 16-27 are unpatentable under 35U.S.C.102(e) as anticipated by Raspanti's '973 patent. In its decision, the Board erroneously held that the Gugumus claims 16-27 were not entitled to the benefit of priority based upon European priority application EP 95810042.2 due to a lack of a written description in the European application of the full scope of the subject matter recited in the Gugumus claims. The Board erroneously failed to recognize that the disclosure of the European application, together with the knowledge of those skilled in the art at the time of the filing of the European application, were sufficient to constitute a sufficient enabling written description of the subject matter of the Gugumus claims pursuant to 35 U.S.C. § 112, first paragraph.

13. CIBA preserves all the issues raised in its motions in the U.S. Patent and Trademark Office as they relate to Count I.

COUNTS

14. This is a Cross-Complaint action pursuant to 35 U.S.C. § 146 and C.F.R. 1.304 that CIBA is entitled to certain patent claims in its application 10/081,291 in interference.

15. CIBA repeats and realleges the allegations contained in paragraphs 1 through 14 of this Complaint as if fully set forth herein.

WHEREFORE, PLAINTIFF prays that the Court grant:

A. Leave to introduce the record of Interference No. 105,262 before the Board and to take discovery and introduce additional evidence to supplement the record in this action;

B. *De novo* consideration by this Court of the Interference record, if introduced, and the supplemental evidence, with respect to the issues of patentability and affirm CIBA's priority

as to Count I and other matters as referenced herein or which CIBA asserts are related to this matter.

C. Judgment awarding priority to Cross-Plaintiff CIBA with respect to Count I.

D. Judgment ordering that:

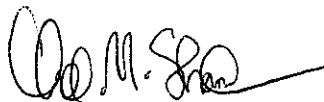
(i) claims 16-27 of the '291 application are patentable to CIBA (Gugumus);

and; that:

(ii) claims 16-27 are entitled to priority based upon the earlier European application EP 95810042.2.

E. That the Clerk of this Court shall issue a certified copy of this court's judgment for transmittal to the U.S. Patent and Trademark Office, and that the Director of the U.S. Patent and Trademark Office shall be authorized fully to implement this Court's order.

F. Judgment ordering any further relief as may be equitable and/or appropriate in order to preserve the rights of CIBA in any further proceedings on remand before the U.S. Patent and Trademark Office.



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Dated: October 10, 2006

Exhibit 1

United States Patent [19]
Raspaniti

[11] **Patent Number:** **5,658,973**
[45] **Date of Patent:** **Aug. 19, 1997**

[54] **COMPOSITIONS FOR THE STABILIZATION OF SYNTHETIC POLYMERS**

[75] **Inventor:** **Giuseppe Raspaniti**, Bergamo, Italy

[73] **Assignee:** **3V Inc.**, Weehawken, N.J.

[21] **Appl. No.:** **507,197**

[22] **Filed:** **Jul. 26, 1995**

[51] **Int. Cl.⁶** **C08K 5/54; C08K 5/3492; C08K 5/3435**

[52] **U.S. Cl.** **524/99; 252/405; 524/100; 524/102; 524/103**

[58] **Field of Search** **524/100, 99, 102, 524/103; 252/405**

[56] **References Cited**

U.S. PATENT DOCUMENTS

4,086,204	4/1978	Cassandrini et al.	544/198
4,108,829	8/1978	Cassandrini et al.	544/198
4,233,412	11/1980	Rody et al.	525/167
4,331,586	5/1982	Hardy	524/97
4,477,615	10/1984	Raspaniti et al.	524/100
4,692,486	9/1987	Gugumus	524/100
4,863,981	9/1989	Gugumus	524/100
4,927,930	5/1990	Cantatore et al.	544/198
4,933,451	6/1990	Cantatore et al.	524/100
5,021,485	6/1991	Gugumus	524/100

FOREIGN PATENT DOCUMENTS

343717	11/1989	European Pat. Off.
57-38589	8/1982	Japan

OTHER PUBLICATIONS

Tomoyuki Kurumada, et al., "Synergism of Hindered Amine Light Stabilizers and UV-Absorbers", *Polymer Degradation and Stability* 19 (1987) 263-272.

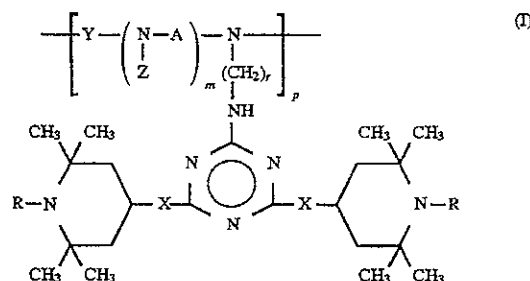
Primary Examiner—Veronica P. Hoke

Attorney, Agent, or Firm—Griffin, Butler, Whisenhunt & Kurtossy

[57] **ABSTRACT**

A composition for stabilizing synthetic polymers consisting of a blend of

a) at least a derivative of a high molecular weight polymethylpiperidine of formula (I)



wherein the groups are as defined hereinafter, and
b) at least one other HALS stabilizer wherein the groups are as defined hereinafter is disclosed. These compositions show photostabilizing and antioxidant properties.

15 Claims, No Drawings

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1

COMPOSITIONS FOR THE STABILIZATION OF SYNTHETIC POLYMERS

The present invention relates to compositions consisting of mixtures of two or more different derivatives of high molecular weight polymethylpiperidine and to their use as stabilizing agents for synthetic polymers.

BACKGROUND OF THE INVENTION

The use of compounds containing the polymethylpiperidine group, and mainly 2,2,6,6-tetramethyl-4-piperidine, for the photostabilization of polymers is well known and to this end a wide literature exists.

Generally this class of stabilizing agents is divided into two groups, namely those having low molecular weight (about 700) and those with high molecular weight (higher than 700).

A detailed disclosure of some stabilizing agents of this class, the so called hindered amines, of their different kinds and of their applicative characteristics is found in Gaechter-Mueller/Taschenbuch der Kunststoff-Additive, 2 Ausgabe 1983 pagg. 144-198.

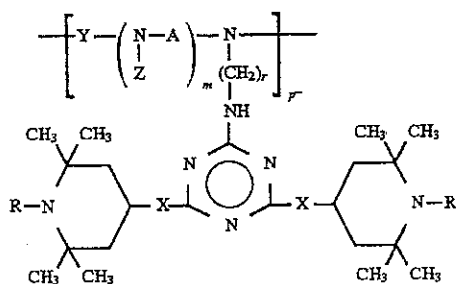
U.S. Pat. Nos. 4,692,486, 5,021,485 and EP 0080431 disclose some synergistic mixtures of derivatives of low and high molecular weight polyalkylpiperidines as photostabilizing agents for polymers. U.S. Pat. No. 4,863,981 discloses also mixtures containing two different derivatives of polymethylpiperidine, both of them having high molecular weight, as photostabilizing agents for polymers.

It has surprisingly been found that new particular combinations of compounds, all of them having high molecular weight, containing polymethylpiperidine groups, in addition to synergistic properties as photostabilizing agents, also show synergistic activity in the long term heat stabilization of synthetic polymers. As used herein, the wording "long term heat stabilization" is intended to mean that the polymer is stabilized against the degradation which occurs during the time of use of the polymer itself. As far as it is known to the applicant, said synergistic activity in the long term heat stabilization was not disclosed nor suggested in the prior art.

DISCLOSURE OF THE INVENTION

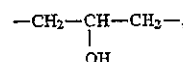
An object of the present invention is a composition for the stabilization of synthetic polymers consisting of a mixture of:

a) at least a compound of formula (I)

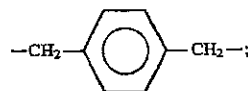


wherein R is hydrogen or methyl, X is oxygen or the N-R₁ group, in which R₁ is hydrogen or a C₁-C₁₂ straight or branched alkyl, r is a number ranging from 2 to 8, included; A is -(CH₂)_n-, in which n can be a number from 2 to 8, the group

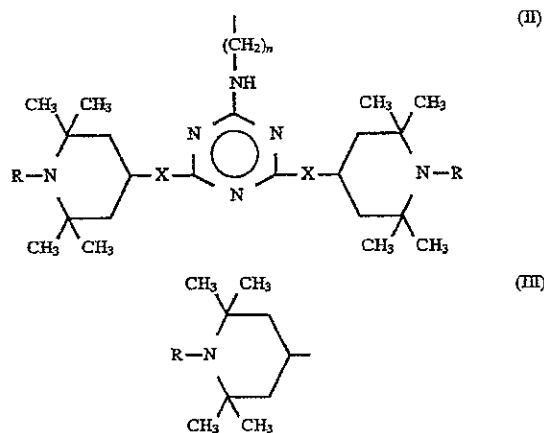
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or the group



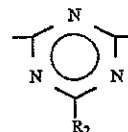
Z is hydrogen, C₁-C₁₈ alkyl, the group of formula (II) or the piperidine of formula (III):



wherein R, X and n have the above defined meaning;

m is zero or 1;

Y, when m is zero, has the same meaning of A, when m is 1 can have the same meaning of A or is one of the following groups



---CO---R₃---CO---; ---CO---NH---R₄---NH---CO--- in which R₂ is an optionally substituted aryl residue, having from 6 to 14 carbon atoms or the

(I)

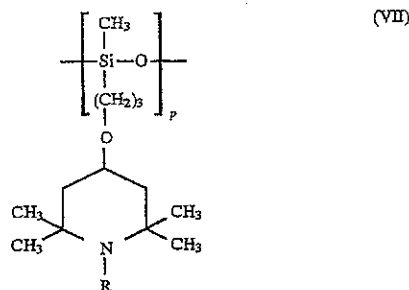
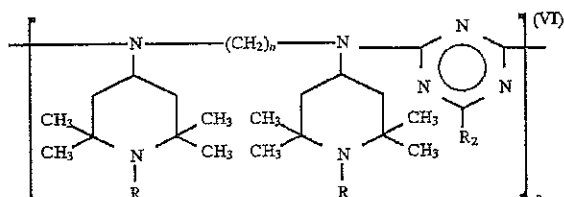
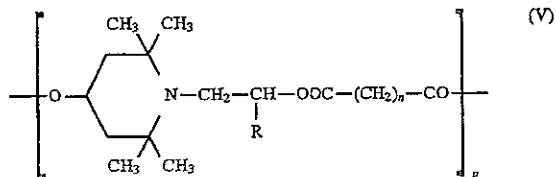
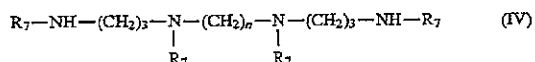
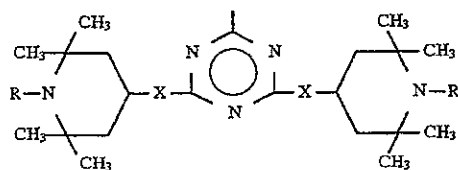


group in which R₅ and R₆ can be the same or different and are hydrogen, a C₁-C₁₈ straight or branched alkyl group, a cycloalkyl group having from 5 to 12 carbon atoms, an aryl group having from 6 to 12 carbon atoms, an aralkyl group having from 7 to 12 carbon atoms; the piperidine group of formula (III) or, together the nitrogen atom which they are linked to, can form a heterocyclic ring having from 5 to 7 members, optionally containing also oxygen as heteroatom; R₃ is phenylene or -(CH₂)_n-; R₄ is toluylene, xylylene or -(CH₂)_n-, in which n has the above defined meaning; p can vary from 2 to 100; the terminal groups can be Cl or H; and

5,658,973

3

b) at least a compound of formula (IV), (V); (VI) or (VII)

wherein R_7 is a group of formula

wherein X and R are as above defined;

R, R_2 , n and p have the above meaning, the terminal groups can be hydrogen for compounds (V), chlorine or hydrogen for compounds (VI) and methyl for compounds (VII).Examples of C_1 - C_{18} straight or branched alkyl group are methyl, ethyl, n-propyl, isopropyl, n-butyl, tert-butyl, pentyl, neo-pentyl, hexyl, heptyl, decyl, dodecyl, hexadecyl, octadecyl.

Examples of optionally substituted aryl group having from 6 to 14 carbon atoms are phenyl, tolyl, o-, m-, p-xylyl.

4

Examples of cycloalkyl group having from 5 to 12 carbon atoms are cyclopentyl, cyclohexyl, cyclododecyl.

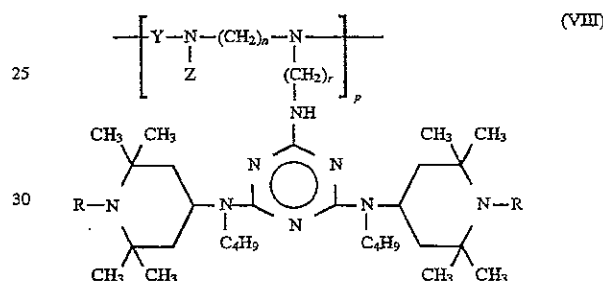
Examples of aralkyl group having from 7 to 12 carbon atoms are benzyl, 4-tert-butylbenzyl.

Examples of heterocyclic group having from 5 to 7 members are: pyrrolidine, piperidine, hexamethyleneimine, morpholine.

The compounds of formula (I), (IV), (V), (VI) and (VII) are known; their methods of preparation as well as their uses as stabilizing agents are described in patents U.S. Pat. Nos. 4,477,615, 4,233,412, 4,108,829, 4,086,204, 4,331,586, EP 0255181.

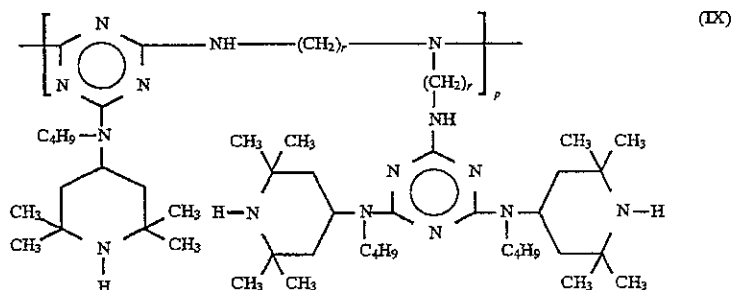
However, the stabilizing compositions according to the present invention show a photoprotective activity higher than the single components of formula (I) or (IV-VII).

In a first preferred embodiment of the present invention, the component a) is represented by the compound of formula (VIII)



wherein Z, Y, R, n and p have the above defined meaning; r is 2 or 3.

In a second preferred embodiment of the present invention, the component a) is represented by the compound of formula (IX)

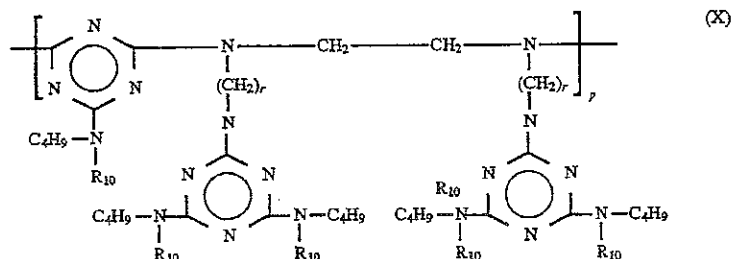


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wherein r and p are as above defined.

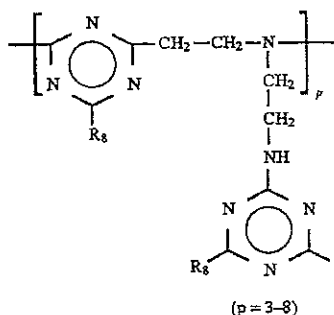
In a third preferred embodiment of the present invention, the component a) is represented by the compound of formula (X)



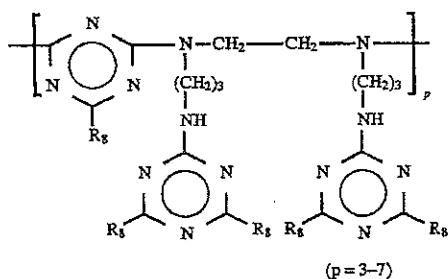
wherein r and p are as above defined, R_{10} is a group of formula (III).

An example of compound of formula IV is:

Examples of compounds of formula I are:

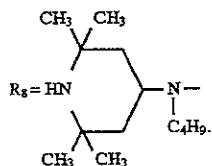


compound 1



compound 2

wherein



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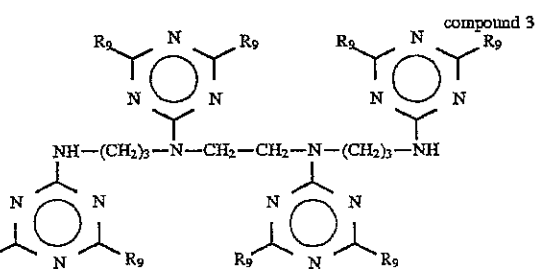
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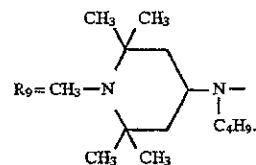
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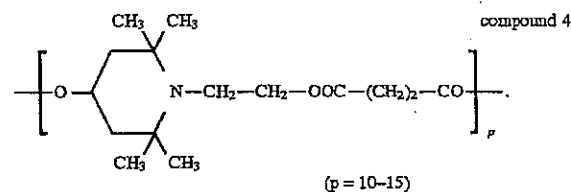
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wherein



An example of compound of formula V is:

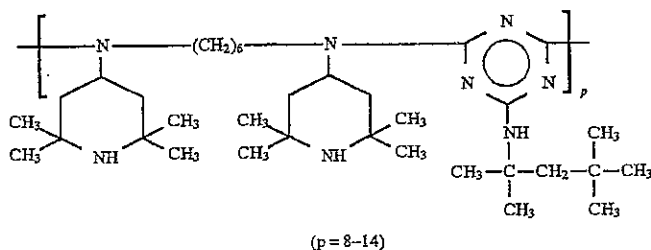


Examples of compounds of formula VI are:

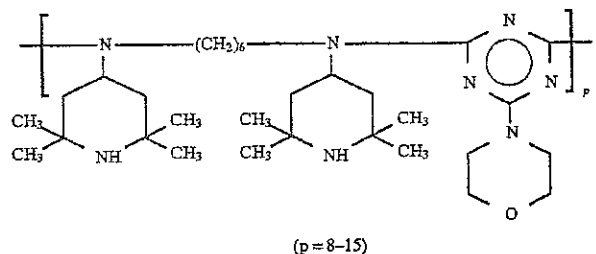
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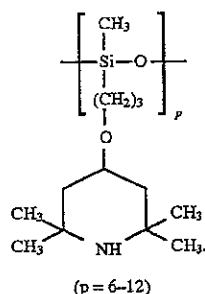


compound 5



compound 6

An example of compound of formula VII is:



compound 7

The concentration of the stabilizing compositions according to the present invention in the polymers can generally vary from 0.01 to 5% and preferably from 0.05 to 2% with respect to the weight of the polymer. Nevertheless, the stabilizing mixture can be added to the polymers also in very high amounts, for example 5-25% by weight, for the preparation of masterbatches.

The incorporation can be carried out according to various methods, for example by dry mixing the polymer with the stabilizing mixture or said mixture can be added to a suspension of the polymer to be stabilized in a suitable solvent and subsequently evaporating off the solvent.

Subsequently the polymers containing the stabilizing mixture are extruded or treated according to methods usually known in the art.

According to the present invention the compositions of compounds of formula (I) and respectively of formula (IV)-(VII) are used for the stabilization of synthetic polymers, particularly of polyolefins such as for example low and high density polyethylene, polypropylene, polymethylpentene, polyisoprene, polystyrene, polymethylstyrene and copolymers thereof and/or with other vinyl monomers as for example acrylonitrile, vinyl acetate, acryl esters.

The stabilizing compositions according to the present invention can be used also together with other additives commonly used in the technology of the synthetic polymers, such as for example: antioxidants, for example those belonging to the classes of phenols, thioethers, phosphites and phosphonites; UV-absorber, for example oxanilides, benzotriazole and benzophenone derivatives; nickel complexes;

metal deactivators, for example oxalic acid amides, plasticizers, antistatic agents, pigments, optical bleaching agents, flame retarders.

The following examples further disclose the present invention.

EXAMPLE 1

1.000 g of low density polyethylene (Riblene EF 2100 V-Bnichem®), 2 g of n-octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, 1 g of calcium stearate and 1 g of a stabilizing agent, according to the present invention, or of a mixture thereof in 50:50 w/w ratio, were mixed homogeneously. The mixtures were extruded at 190° C. and transformed into pellets. From these pellets, by means of pressure forming at 200° C., films of 0.2 mm thickness were obtained.

Samples of these films were subjected to UV radiation in a Weatherometer WOM Ci-65® at a black panel temperature of 63° C. In the irradiated samples the increase of the carbonyl band at 5.85 nm in the infrared was measured and the T-0.1, i.e. the time necessary to give an increase of 0.1 of the carbonyl band, was determined. The results are reported in the following Table 1.

TABLE 1

Stabilizing agent	T 0.1 (hours)
Without stabilizing agent	300
Compound 1	2100
Compound 2	2000
Compound 3	1950
Compound 4	1750
Compound 5	2100
Compound 7	1650
Compounds 1 + 3	2750
Compounds 1 + 4	2850
Compounds 1 + 5	2650
Compounds 2 + 5	2800
Compounds 1 + 7	2600
Compounds 4 + 5 (according to US 4 863 981)	2800

EXAMPLE 2

Homogeneous mixtures, consisting of 1,000 g of polypropylene, (Moplen FLF 20-Himont®), 1 g of 1,3,5-tris-(3,5-di-tert-butyl-4-hydroxybenzyl)isocyanurate, 0.5 g

5,658,973

9

of calcium stearate and 2 g of a stabilizing agent or of a 50:50 mixture thereof were prepared. The mixtures were extruded at 250° C. and granulated. From these, by means of pressure forming at 260° C., 1 mm thickness-test pieces were obtained.

The so obtained test pieces were subjected to atmospheric oxygen action by heating at 130° C. in a forced air circulation oven.

The degradation was evaluated by determining the time necessary for the "chalky" appearance on test pieces.

The results are reported in the following Table 2.

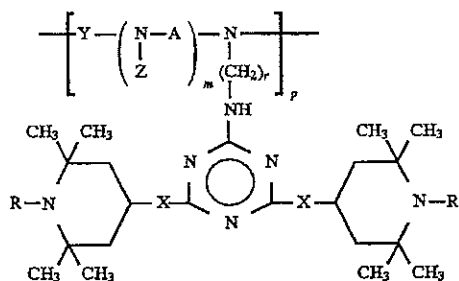
TABLE 2

Stabilizing agent	T (days)
Without stabilizing agent	34
Compound 1	53
Compound 2	57
Compound 3	49
Compound 4	54
Compound 5	57
Compound 7	41
Compounds 1 + 3	85
Compounds 2 + 4	81
Compounds 1 + 5	80
Compounds 2 + 5	78
Compounds 1 + 7	76
Compounds 4 + 5 (according to US 4 863 981)	58

I claim:

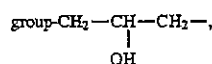
1. A composition for the stabilization of synthetic polymers comprising an about 1:1 ratio of the following components a) and b) wherein:

a) is at least one compound of formula (I)

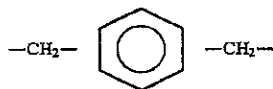


wherein R is hydrogen or methyl, X is oxygen or the group N—R₁, in which R₁ is hydrogen or C₁–C₁₂ straight or branched alkyl group, r is a number ranging from 2 to 8, included;

A is —(CH₂)_n—, in which n can be a number from 2 to 8, the

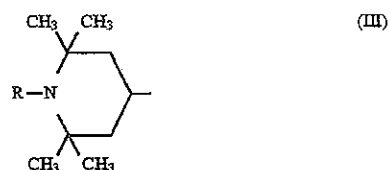
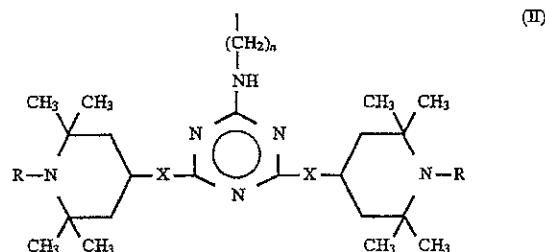


or the group



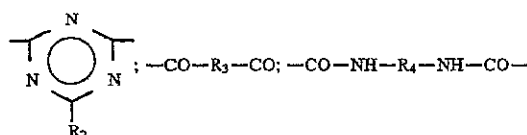
Z is hydrogen, C₁–C₁₈ alkyl, the group of formula (II) or the piperidine of formula (III)

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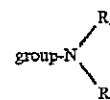


wherein R, X and n have the meaning above defined; m is zero or 1;

Y, when m is zero, has the same meaning of A, when m is 1 can have the same meaning of A or is one of the following groups



in which R₂ is an optionally substituted aryl residue, having from 6 to 14 carbon atoms or the



in which R₅ and R₆ can be the same or different and are hydrogen, a C₁–C₁₈ straight or branched alkyl group, a cycloalkyl group having from 5 to 12 carbon atoms, an aryl group having from 6 to 12 carbon atoms, an aralkyl group having from 7 to 12 carbon atoms; the piperidine group of formula (III) or, together the nitrogen atom, can form a 5 to 7 member heterocyclic ring, optionally containing oxygen as heteroatom;

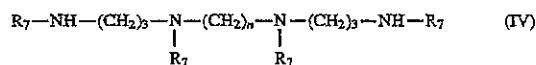
R₃ is phenylene or —(CH₂)_n—;

R₄ is toluylene, xylylene or —(CH₂)_n—, in which n has the above defined meaning,

p can range from 2 to 100;

the terminal groups can be Cl or H; and

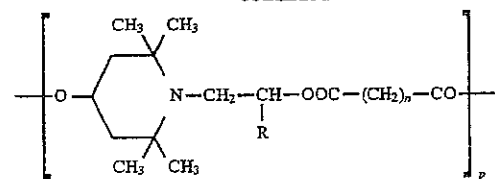
b) is at least one compound of formula (IV), (V); (VI) or (VII)



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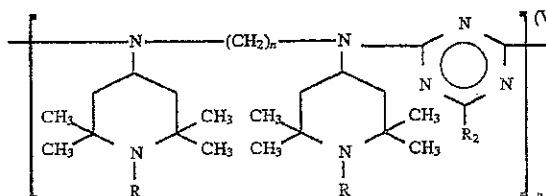
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(V)

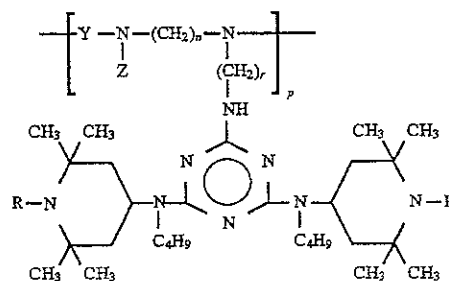
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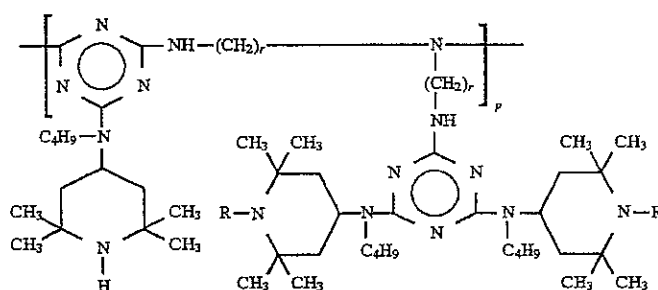
12



(VIII)

wherein Z, Y, R, n and p are as above defined, r is 2 or 3.

3. A composition according to claim 1, wherein said compound a) is a compound of formula (IX), and said compound b) is a compound of formula (IV)-(VII)

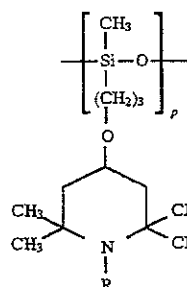
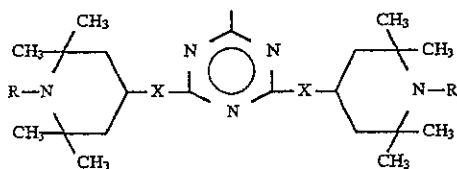


(IX)

wherein r and p are as above defined.

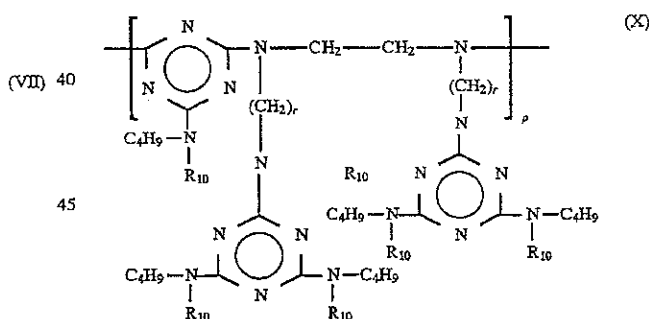
4. A composition according to claim 1, wherein a) is a compound of formula (X) and b) is a compound of formula (IV)-(VII)

-continued

wherein R₇ is a group of formula

wherein R, X, n and p are as above identified.

2. A composition according to claim 1, wherein said compound a) is a compound of formula (VIII), and said compound b) is a compound of formula (IV)-(VII)

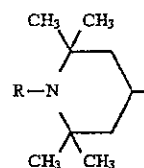


(VII)

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wherein r and p are as above defined and R₁₀ is a group of formula (III)

(III)

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wherein R is as above defined.

5. Masterbatch for the stabilization of synthetic polymers containing from 5 to 25% by weight of composition of claim 1.

6. A composition according to claim 1, consisting of a) and b).

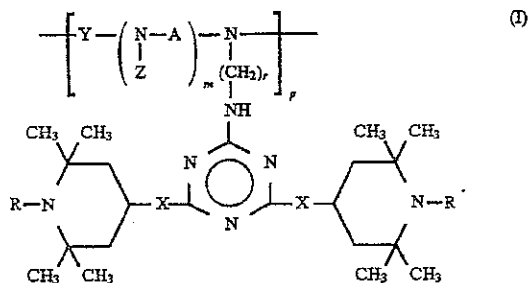
7. A method for stabilizing synthetic polymers, comprising the step of adding to a polyolefin an effective stabilizing

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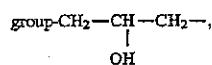
amount of a composition comprising an about 1:1 ratio of the following components a) and b) wherein:

a) is at least one compound of formula (I)

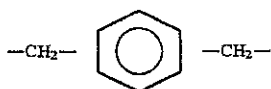


wherein R is hydrogen or methyl, X is oxygen or the group N—R₁, in which R₁ is hydrogen or C₁–C₁₂ straight or branched alkyl group, r is a number ranging from 2 to 8, included;

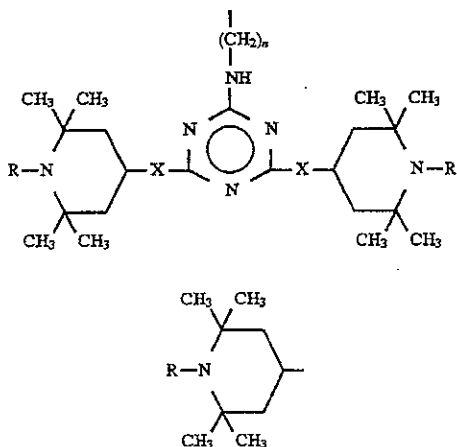
A is —(CH₂)_n—, in which n can be a number from 2 to 8, the



or the group



Z is hydrogen, C₁–C₁₈ alkyl, the group of formula (II) or the piperidine of formula (III)

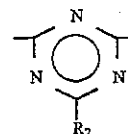


wherein R, X and n have the meaning above defined;

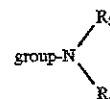
m is zero or 1;

Y, when m is zero, has the same meaning of A, when m is 1 can have the same meaning of A or is one of the following groups

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—CO—R₃—CO; —CO—NH—R₄—NH—CO— in which R₂ is an optionally substituted aryl residue, having from 6 to 14 carbon atoms or the



in which R₅ and R₆ can be the same or different and are hydrogen, a C₁–C₁₈ straight or branched alkyl group, a cycloalkyl group having from 5 to 12 carbon atoms, an aryl group having from 6 to 12 carbon atoms, an aralkyl group having from 7 to 12 carbon atoms; the piperidine group of formula (III) or, together the nitrogen atom, can form a 5 to 7 member heterocyclic ring, optionally containing oxygen as heteroatom;

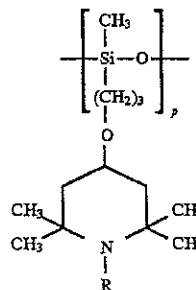
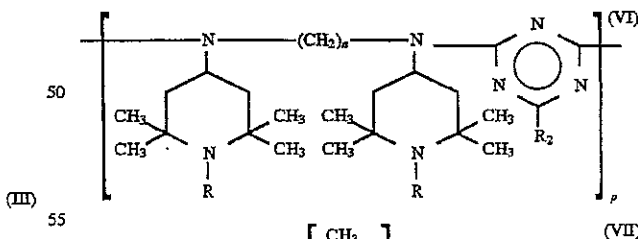
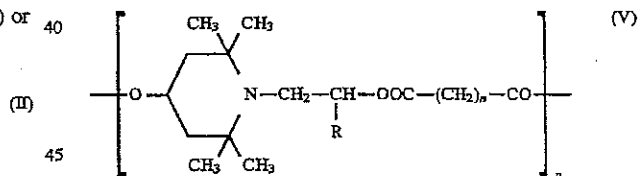
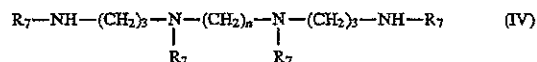
R₃ is phenylene or —(CH₂)_n—;

R₄ is toluylene, xylylene or —(CH₂)_n—, in which n has the above defined meaning,

p can range from 2 to 100;

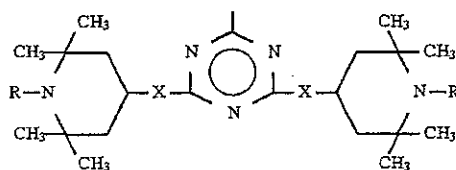
the terminal groups can be Cl or H; and

b) at least a compound of formula (IV), (V); (VI) or (VII)



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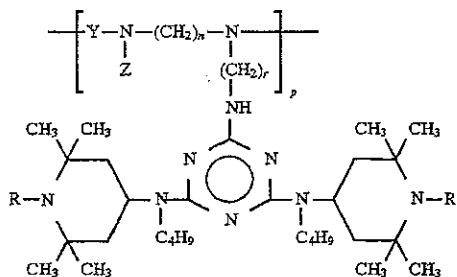
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wherein R₇ is a group of formula

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wherein R, X, n and p are as above identified.

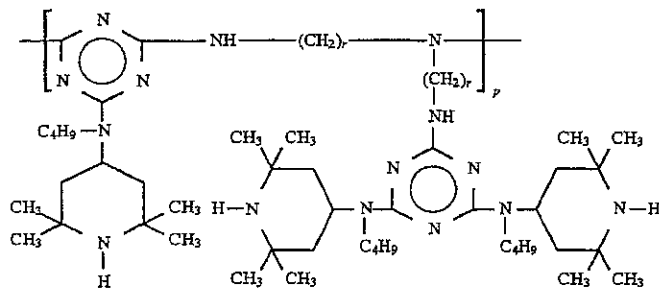
8. A method for stabilizing synthetic polymers, according to claim 7, wherein said compound a) is a compound of formula (VIII),



(VIII)

wherein X, Y, R, n and p are as above defined, r is 2 or 3.

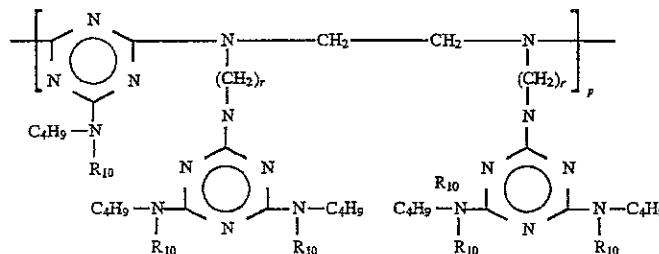
9. A method according to claim 7, wherein said compound a) is a compound of formula (IX), and said compound b) is a compound of formula (IV)-(VII)



(IX)

wherein r and p are as above defined.

10. A method according to claim 7, wherein a) is a compound of formula (X) and b) a compound of formula (IV)-(VII)

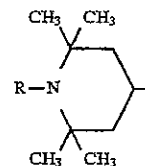


(X)

wherein r and p are as above defined and R₁₀ is a group of formula (III)

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(III)

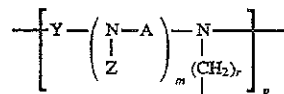


wherein R is as above defined.

11. A stabilized polymer comprising a polyolefin and a composition for the stabilization of synthetic polymers comprising an about 1:1 ratio of the following components a) and b) wherein:

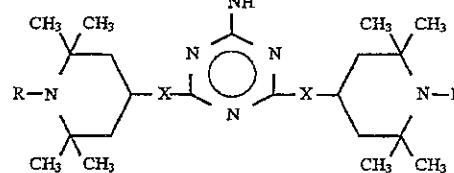
a) is at least one compound of formula (I)

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(I)

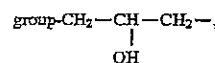
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wherein R is hydrogen or methyl, X is oxygen or the group N-R₁, in which R₁ is hydrogen or C₁-C₁₂ straight or branched alkyl group, r is a number ranging from 2 to 8, included;

A is -(CH₂)_n-, in which n can be a number from 2 to 8, the

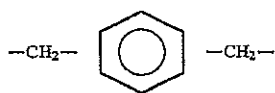


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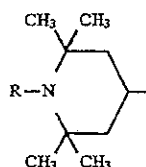
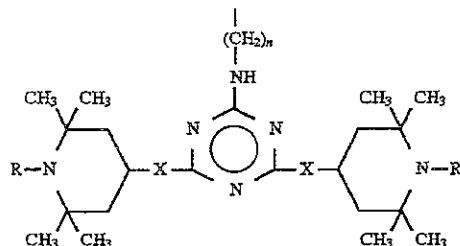
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or the group

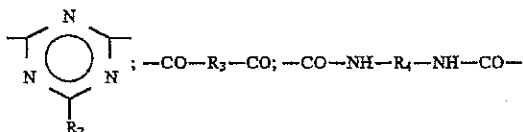


Z is hydrogen, C₁-C₁₈ alkyl, the group of formula (II) or the piperidine of formula (III)

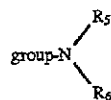


wherein R, X and n have the meaning above defined;
m is zero or 1;

Y, when m is zero, has the same meaning of A, when m is 1 can have the same meaning of A or is one of the following groups



in which R₂ is an optionally substituted aryl residue, having from 6 to 14 carbon atoms or the



in which R₅ and R₆ can be the same or different and are hydrogen, a C₁-C₁₈ straight or branched alkyl group, a cycloalkyl group having from 5 to 12 carbon atoms, an aryl group having from 6 to 12 carbon atoms, an aralkyl group having from 7 to 12 carbon atoms; the piperidine group of formula (III) or, together the nitrogen atom, can form a 5 to 7 member heterocyclic ring, optionally containing oxygen as heteroatom;

R₃ is phenylene or $-(\text{CH}_2)_n-$;

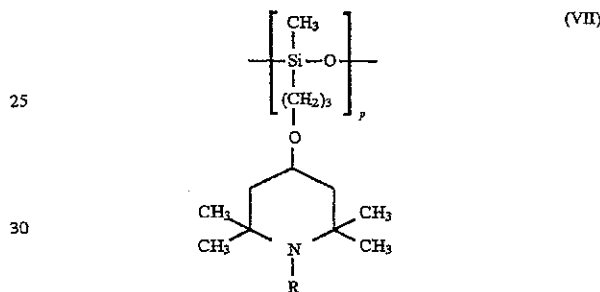
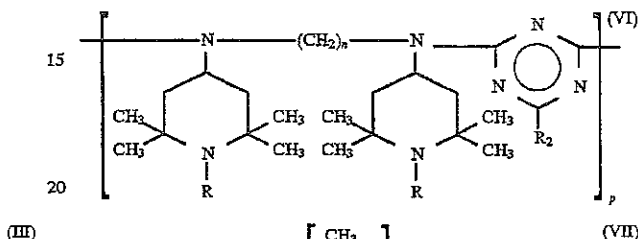
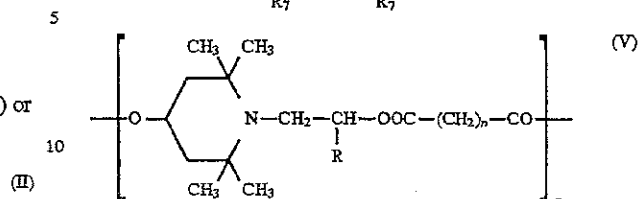
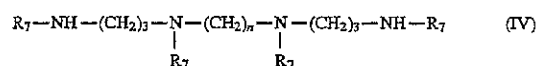
R₄ is toluylene, xylylene or $-(\text{CH}_2)_n-$, in which n has the above defined meaning,

p can range from 2 to 100;

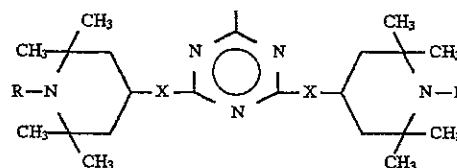
the terminal groups can be Cl or H; and

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b) at least a compound of formula (IV), (V); (VI) or (VII)

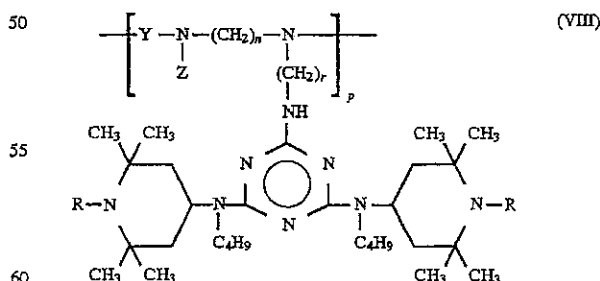


wherein R₇ is a group of formula



wherein R, X, n and p are as above identified.

12. A stabilized polymer according to claim 11 wherein said compound a) is a compound of formula (VIII), and said compound b) is a compound of formula (IV)-(VII)



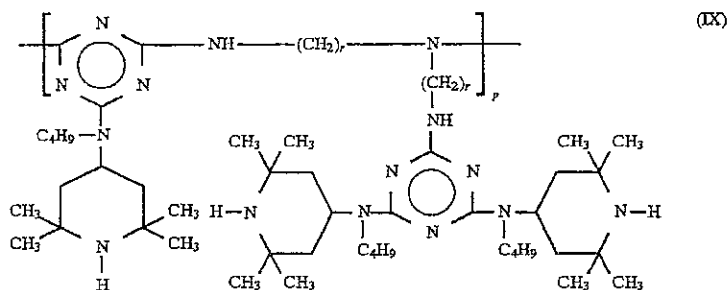
wherein Z, Y, R, n and p are as above defined, r is 2 or 3.

13. A stabilized polymer according to claim 11 wherein said compound a) is a compound of formula (IX), and said compound b) is a compound of formula (IV)-(VII)

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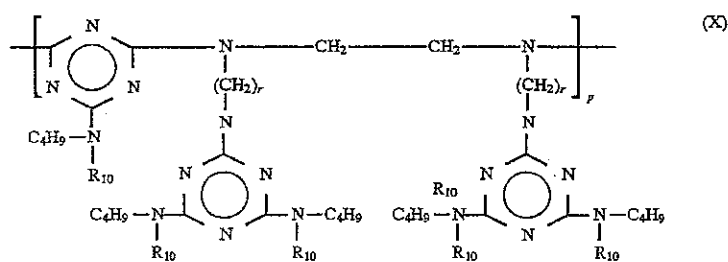


wherein r and p are as above defined.

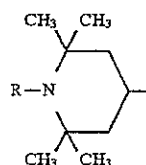
14. A stabilized polymer according to claim 11 wherein a) is a compound of formula (X) and b) is a compound of formula (IV)-(VII)

15 wherein R is as above defined.

15. A stabilized polymer according to claim 11 wherein said composition is present in an amount from 0.01 to 5% w-w.



wherein r and p are as above defined and R_{10} is a group of formula (III)



(III) 35

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Exhibit 2

US 20020120042A1

(12) **Patent Application Publication**
Gugumus

(43) Pub. Date: Aug. 29, 2002

(76) Inventor. Francois Gugumus, Allschwil (CH)

$$\left[\text{O} - \text{C}_6\text{H}_2(\text{CH}_3)_4 - \text{N} - \text{CH}_2 - \underset{\text{R}_1}{\text{CH}} - \text{OOC} - \text{R}_2 - \text{CO} \right]_n$$

(22) Filed Feb. 22, 2002

Revised U.S. Application Data

$$\left[\text{CH}_2 - \underset{\text{OH}}{\text{CH}} - \text{CH}_2 - \underset{\text{N}}{\text{C}} \begin{array}{c} \text{H}_3\text{C} \quad \text{CH}_3 \\ \text{H}_3\text{C} \quad \text{CH}_3 \end{array} \begin{array}{c} \text{O} \\ \text{C} \\ \text{O} \end{array} \begin{array}{c} \text{CH}_2 \\ \text{CH}_2 \end{array} (\text{CH}_2)_{19} \right]_n \quad (11a)$$

(30) Foreign Application Priority Data

JAN. 23, 1995 (EP) 95810042.2

Publication Classification

(51) Int. Cl.⁷ **.. C08K 5/34**
(52) U.S. Cl. **.. 524/102**

(57) ABSTRACT

A synergistic stabilizer mixture comprising a component a) and, for example, a component b), where component a) is at least one compound of the formula I

in which n_1 and n_2 are a number from 2 to 50.

US 2002/0120042 A1

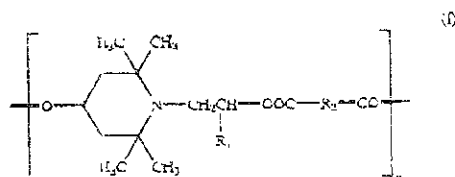
Aug. 29, 2002

SYNERGISTIC STABILIZER MIXTURE

[0001] The present invention relates to a stabilizer system comprising two specific high-molecular-weight polyalkylpiperidine derivatives, to the use of this stabilizer system for stabilizing organic material, and to the organic material protected against thermal, oxidative or light-induced degradation by means of the stabilizer system mentioned. U.S. Pat. No. 6,924,880, U.S. Pat. No. 4,863,981, U.S. Pat. No. 4,957,953, WO-A-92/12 201, EP-A-449 685, EP-A-632 092, GB-A-2 277 499 and Research Disclosure 34549 (January 1993) describe stabilizer mixtures comprising two polyalkylpiperidine derivatives.

[0002] The present invention relates to a stabilizer mixture comprising a component a) and a component b), c), d) or e), where

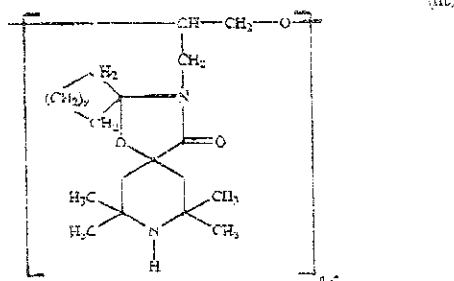
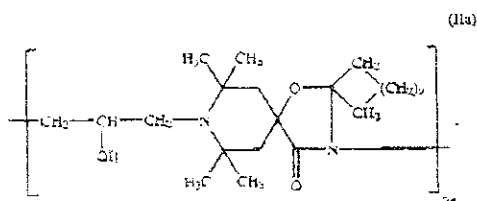
[0003] component a) is at least one compound of the formula I:



[0004] in which R_1 is hydrogen or methyl,

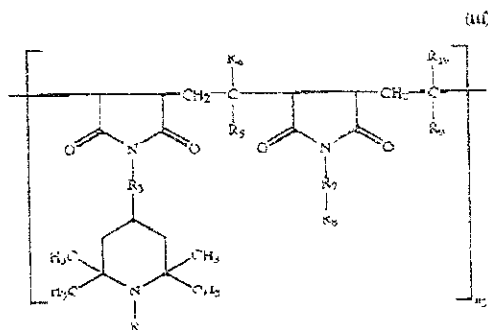
[0005] R_2 is a direct bond or C_1 - C_{30} alkylene and n_1 is a number from 2 to 50,

[0006] component b) is at least one compound of the formula IIa and IIb:

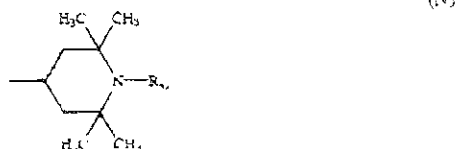


[0007] in which n_2 and n_3 are a number from 2 to 50,

[0008] component c) is at least one compound of the formula III:



[0009] in which R_5 and R_7 , independently of one another, are a direct bond or an $-\text{N}(\text{X}_1)-\text{CO}-\text{X}_2-\text{CO}-\text{N}(\text{X}_3)-$ group, where X_1 and X_3 , independently of one another, are hydrogen, C_1 - C_6 alkyl, C_5 - C_{10} cycloalkyl, phenyl, C_7 - C_9 phenylalkyl or a group of the formula IV:



[0010] and X_2 is a direct bond or C_1 - C_4 alkylene, R_1 is hydrogen, C_1 - C_6 alkyl, O , $-\text{CH}_2\text{CN}$, C_3 - C_6 alkenyl, C_7 - C_9 phenylalkyl, C_7 - C_9 phenylalkyl which is substituted by C_1 - C_6 alkyl on the phenyl radical, or C_3 - C_6 acyl,

[0011] R_5 , R_6 , R_7 and R_8 , independently of one another, are hydrogen, C_1 - C_{30} alkyl, C_5 - C_{10} cycloalkyl or phenyl,

[0012] R_9 is hydrogen, C_1 - C_{30} alkyl, C_5 - C_{10} cycloalkyl, C_7 - C_9 phenylalkyl, phenyl or a group of the formula IV, and

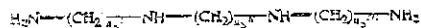
[0013] n_4 is a number from 1 to 50,

[0014] component d) is at least one compound of the formula V:

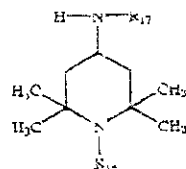
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$$\left[\begin{array}{c} \text{O} \\ \parallel \\ \text{C} - \text{R}_{11} - \text{CH}_2 - \text{N}_{12} - \text{CH} - \text{R}_{13} - \text{C}(=\text{O}) - \text{O} - \text{R}_{14} - \text{C}_{10}\text{H}_6 - \text{O} - \text{R}_{15} - \text{O} \end{array} \right]_n \quad (V)$$

$\begin{array}{c} \text{O} \\ \parallel \\ \text{C} \\ | \\ \text{O} \\ | \\ \text{C}_6\text{H}_4 \\ | \\ \text{N}(\text{R}_{16})_2 \end{array} \quad \begin{array}{c} \text{O} \\ \parallel \\ \text{C} \\ | \\ \text{O} \\ | \\ \text{C}_6\text{H}_4 \\ | \\ \text{N}(\text{R}_{16})_2 \end{array}$

(VI₂)

MDI



[0020] Examples of alkyl having up to 30 carbon atoms are methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, 2-ethylbutyl, n-pentyl, isopentyl, 1-methylpentyl, 1,3-dimethylbutyl, n-hexyl, 1-methylhexyl, n-heptyl, isohexyl, 1,1,3,3-tetramethylbutyl, 1-methylheptyl, 3-methylheptyl, n-octyl, 2-ethylhexyl, 1,1,3-trimethylhexyl, 1,1,3,3-tetramethylpentyl, nonyl, decyl, undecyl,

[1030] Component a) can be prepared analogously to known processes, for example by reaction of a polyamine of the formula VIa with cyanate chloride in a molar ratio of from 1:2 to 1:4 in the presence of anhydrous lithium carbonate, sodium carbonate or potassium carbonate in an organic solvent, such as 1,2-dichloroethane, toluene, xylene,

US 2002/0120042 A1

Aug. 29, 2002

3

benzene, dioxane or tert-amyl alcohol, at a temperature of from -20°C . to $+10^{\circ}\text{C}$., preferably from -10°C . to $+10^{\circ}\text{C}$., in particular from 0°C . to $+10^{\circ}\text{C}$., for from 2 to 8 hours, followed by reaction of the resultant product with a 2,2,6,6-tetramethyl-4-piperidylamine of the formula VIb. The molar ratio between 2,2,6,6-tetramethyl-4-piperidylamine and polyamine of the formula VIa is, for example, from 4:1 to 8:1. The amount of 2,2,6,6-tetramethyl-4-piperidylamine can be added in one portion or in more than one portion at intervals of a few hours.

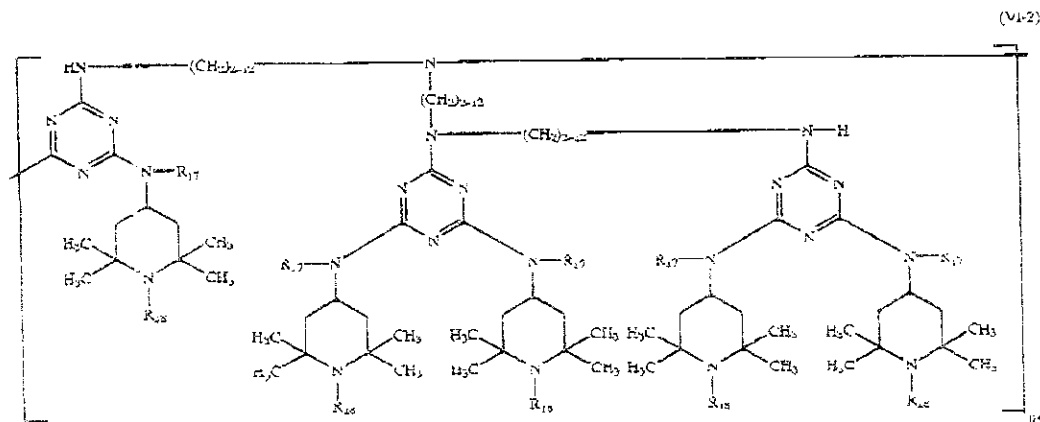
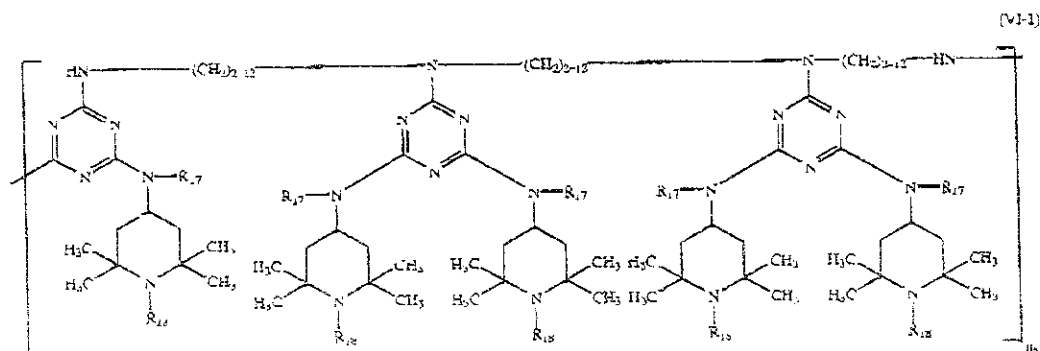
[0031] The polyamine of the formula VIa, cyanuric chloride 2,2,6,6-tetramethylpiperidylamine of the formula VIb ratio is preferably from 1:3.5 to 1:5.6

[0032] The following example indicates one way of preparing the preferred component c).

[0033] Example: 23.6 g (0.128 mol) of cyanuric chloride, 7.43 g (0.0426 mol) of N,N' -bis[3-aminopropyl]ethylenediamine and 18 g (0.13 mol) of anhydrous potassium carbonate are reacted at 5°C . for 3 hours with stirring in 250 ml

of 1,2-dichloroethane. The mixture is warmed at room temperature for a further 4 hours. 27.2 g (0.128 mol) of N -(2,2,6,6-tetramethyl-4-piperidyl)butylamine are added, and the resultant mixture is warmed at 60°C . for 3 hours. A further 18 g (0.13 mol) of anhydrous potassium carbonate are added, and the mixture is warmed at 60°C . for a further 6 hours. The solvent is removed by distillation under a slight vacuum (200 mbar) and replaced by xylene. 18.2 g (0.085 mol) of N -(2,2,6,6-tetramethyl-4-piperidyl)butylamine and 5.2 g (0.13 mol) of ground sodium hydroxide are added, the mixture is refluxed for 2 hours and the water formed during the reaction is removed by azeotropic distillation over a further 12 hours. The mixture is filtered. The solution is washed with water and dried over Na_2SO_4 . The solvent is evaporated, and the residue is dried at 120 - 130°C . in vacuo (0.1 mbar). Component c) is obtained as a colourless resin.

[0034] In general, component c) can be represented for example by a compound of the formula VI-1, VI-2 or VI-3. It can also be in the form of a mixture of these three compounds.



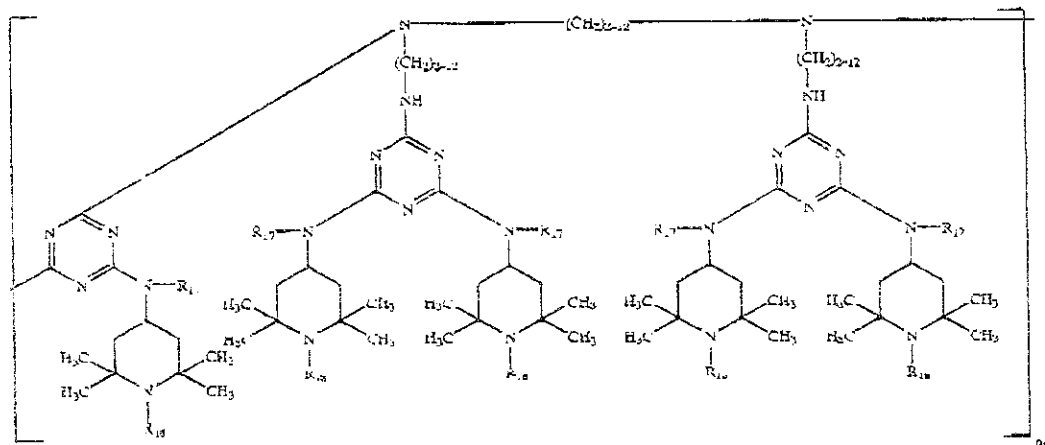
US 2002/01:0042 A1

Aug. 29, 2002

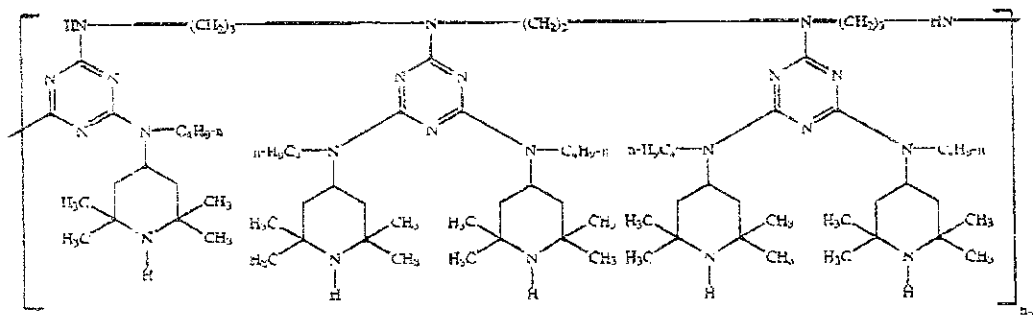
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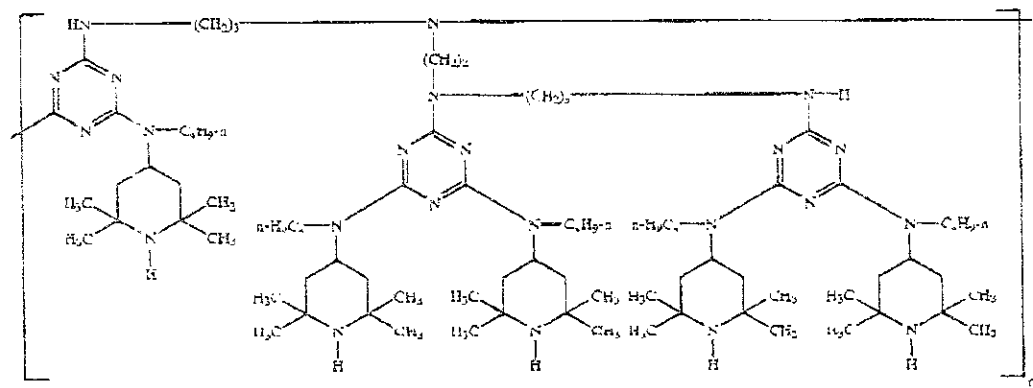
(VI-1)



A preferred meaning of the formula VI-1 is



A preferred meaning of the formula VI-2 is

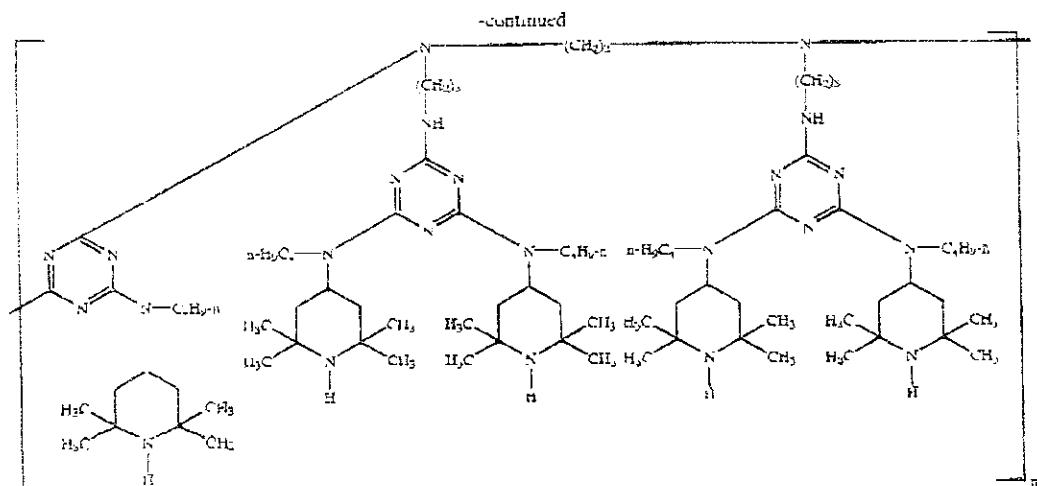


A preferred meaning of the formula VI-3 is

US 2002/0120042 A1

Aug. 29, 2002

5



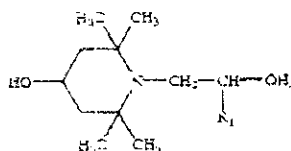
[0035] In the above formulae VI-1 to VI-3, n_3 is preferably 1 to 20.

[0036] Component a) is preferably @TINUVIN 622, component b) is preferably @HOSTAVIN N 30, component c) is preferably @UVINUL 5050 H, @LICHTSCHUTZSTOFF UV 31 or @LUCHEM B 18, component d) is preferably @MARK LA 63 or @MARK LA 68 and component e) is preferably @UVASORB HA 88.

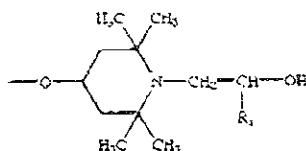
[0037] The compounds of the formulae IIa and IIb can be obtained together as a mixture and also employed as such as component b) in the novel stabilizer system. The IIa, IIb ratio is, for example, from 20:1 to 1:20 or from 1:10 to 10:1.

[0038] The meanings of the terminal groups which saturate the free valences in the compounds of the formulae I, IIa, IIb, III, IV, V, VI-1, VI-2 and VI-3 depend on the processes used for their preparation. The terminal groups can also be modified after the preparation of the compounds.

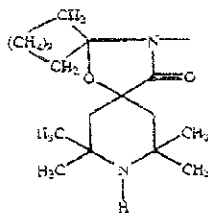
[0039] If the compounds of the formula I are prepared, for example, by reacting a compound of the formula



[0040] in which R_1 is hydrogen or methyl, with a dicarboxylic acid anhydride of the formula $Y-OOC-R_2-COO-Y$, in which Y is, for example, methyl, ethyl or propyl, and R_2 is as defined above, the terminal group bonded to the 2,2,6,6-tetramethyl-4-piperidine-1-yl radical is hydrogen or $-COO-R_2-COO-Y$, and the terminal group bonded to the diacyl radical is $-O-Y$ or



[0041] In the compounds of the formula IIa, the terminal group bonded to the nitrogen can be, for example, hydrogen and the terminal group bonded to the 2-hydroxypropylene radical can be, for example, a



[0042] group.

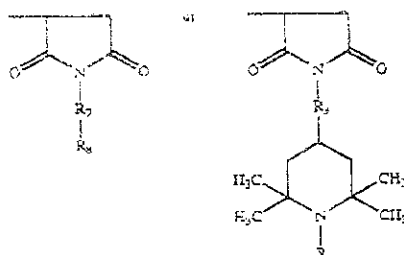
[0043] In the compounds of the formula IIb, the terminal group bonded to the dimethylene radical can be, for example, $-OH$, and the terminal group bonded to the oxygen can be, for example, hydrogen. The terminal groups can also be polyether radicals.

[0044] In the compounds of the formula III, the terminal group bonded to the 2,5-dioxypiperidine ring is, for example, hydrogen, and the terminal group bonded to the $-C(R_9)(R_{10})-$ radical is, for example,

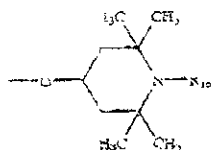
US 2002/01:0042 A1

6

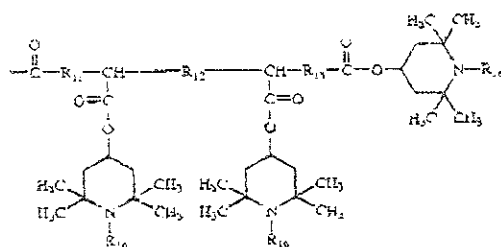
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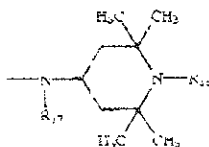
[0045] In the compounds of the formula V, the terminal group bonded to the carbonyl radical is, for example,



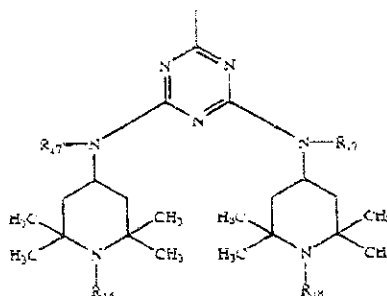
[0046] and the terminal group bonded to the oxygen radical is, for example,



[0047] In the compounds of the formulae VI-1, VI-2 and VI-3, the terminal group bonded to the triazine radical is, for example, Cl or a



[0048] group, and the terminal group bonded to the amino radical is, for example, hydrogen or a

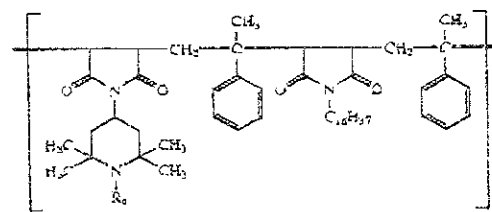
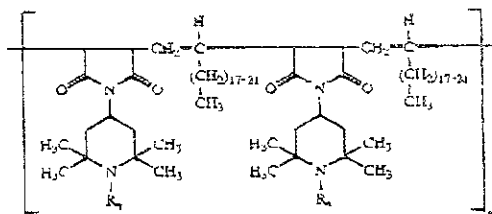


[0049] group

[0050] Preference is given to a stabilizer mixture in which R₁ is hydrogen, R₂ is ethylene, and n₁ is a number from 2 to 25

[0051] Preference is likewise given to a stabilizer mixture in which R₂ and R₇ are a direct bond or an —N(X₁)—CO—X₂—CO—N(X₂)— group, where X₁ and X₂, independently of one another, are hydrogen or C₁–C₄ alkyl and X₂ is a direct bond, R₄ is hydrogen, C₁–C₄ alkyl, OH, C₂–C₁₂ alkoxy, C₅–C₈ cycloalkoxy, allyl, benzyl or acetyl, R₅ and R₆ are C₁–C₂₅ alkyl or phenyl, R₈ and R₁₀ are hydrogen or C₁–C₄ alkyl, R₉ is C₁–C₂₅ alkyl or a group of the formula IV, R₁₁, R₁₅, R₁₆ and R₁₇ are C₁–C₄ alkylene, R₁₂ is a direct bond, and R₁₄ is as defined for R₁.

[0052] Preference is also given to a stabilizer mixture in which component c) is at least one compound of the formula

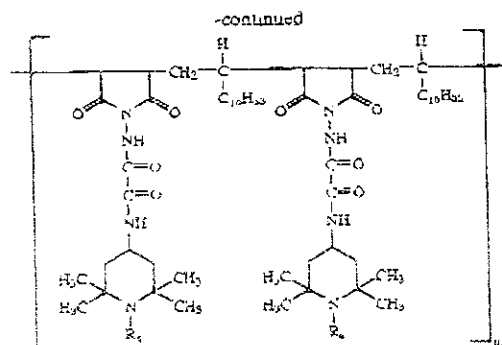


or

US 2002/0120042 A1

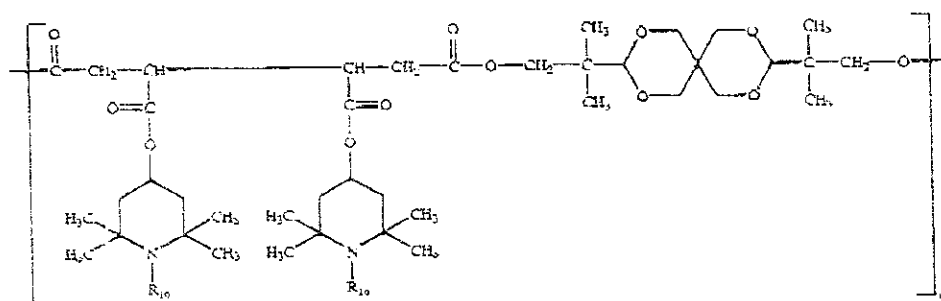
Aug. 29, 2002

7



[0053] in which R_1 is hydrogen or methyl, and n_1 is a number from 1 to 50

[0054] Component d) is preferably at least one compound of the formula



[0055] in which R_{10} is hydrogen or methyl, and n_2 is a number from 1 to 50

[0056] A stabilizer mixture comprising components a) and b) is preferred. Likewise preferred is a stabilizer mixture comprising components a) and c) and a stabilizer mixture comprising components a) and d). Particular preference is given to a stabilizer mixture comprising components a) and c).

[0057] n_1 is preferably from 5 to 20, n_2 and n_3 are preferably from 2 to 10, and n_4 , n_5 and n_6 are preferably from 1 to 10.

[0058] The following stabilizer systems are particularly preferred embodiments of the invention

[0059] 1) stabilizer mixture comprising ③NUVIN 622 and ③HIOSTAVIN N 30,

[0060] 2) stabilizer mixture comprising ③NUVIN 622 and ③UVINUL 5050 H,

[0061] 3) stabilizer mixture comprising ③TINUVIN 622 and ③LICHTSCHUTZSTOFF UV 31,

[0062] 4) stabilizer mixture comprising ③TINUVIN 622 and ③LUCHEM B 18,

[0063] 5) stabilizer mixture comprising ③TINUVIN 622 and ③MARK LA 63,

[0064] 6) stabilizer mixture comprising ③TINUVIN 622 and ③MARK LA 68 and

[0065] 7) stabilizer mixture comprising ③TINUVIN 622 and ③UVASORB HA 88

[0066] The novel stabilizer mixture is suitable for stabilizing organic materials against thermal, oxidative or light-induced degradation. Examples of such materials are the following:

[0067] 1) Polymers of monoolefins and diolefins, for example polypropylene, polyisobutylene, polybut-1-ene, poly-4-methylpent-1-ene, polyisoprene or polybutadiene, as well as polymers of cycloolefins, for instance of cyclopentane or norbornene, polyethylene (which optionally can be crosslinked), for example high density polyethylene (HDPE), high density and high molecular weight polyethylene (HDPE-HMW), high density and ultrahigh molecular weight polyethylene (HDPE-UHMW), medium density polyethylene (MDPE), low density polyethylene (LDPE),

linear low density polyethylene (LLDPE), branched low density polyethylene (BLDPE)

[0068] Polyolefins, i.e. the polymers of monoolefins exemplified in the preceding paragraph, preferably polyethylene and polypropylene, can be prepared by different, and especially by the following, methods

[0069] a) radical polymerisation (normally under high pressure and at elevated temperature)

[0070] b) catalytic polymerisation using a catalyst that normally contains one or more than one metal of groups IVb, Vb, Vlb or VIH of the Periodic Table. These metals usually have one or more than one ligand, typically oxides, halides, alcohols, esters, ethers, amines, alkyls, alkenyls and/or aryls that may be either π - or σ -coordinated. These metal complexes may be in the free form or fixed on substrates, typically on activated magnesium chloride, titanium(III) chloride, alumina or silicon oxide. These catalysts may be soluble or insoluble in the polymerisation medium. The catalysts can be used by themselves in the polymerisation or further activators may be used, typically metal alkyls, metal

US 2002/0120042 A1

Aug. 29, 2002

8

hydrides, metal alkyl halides, metal alkyl oxides or metal alkyl oxanes, said metals being elements of groups Ia, IIa and/or IIIa of the Periodic Table. The activators may be modified conveniently with further ester, ether, amine or silyl ether groups. These catalyst systems are usually termed Phillips, Standard Oil Indiana, Ziegler (-Natta), TNZ (DuPont), metallocene or single site catalysts (SSC).

[0071] 2. Mixtures of the polymers mentioned under 1), for example mixtures of polypropylene with polyisobutylene, polypropylene with polyethylene (for example PP/HDPE, PP/LDPE) and mixtures of different types of polyethylene (for example LDPE/HDPE).

[0072] 3. Copolymers of monolefins and diolefins with each other or with other vinyl monomers, for example ethylene/propylene copolymers, linear low density polyethylene (LLDPE) and mixtures thereof with low density polyethylene (LDPE), propylene/but-1-ene copolymers, propylene/isobutylene copolymers, ethylene/but-1-ene copolymers, ethylene/hexene copolymers, ethylene/methylpentene copolymers, ethylene/heptene copolymers, ethylene/octene copolymers, propylene/butadiene copolymers, isobutylene/isoprene copolymers, ethylene/alkyl acrylate copolymers, ethylene/alkyl methacrylate copolymers, ethylene/vinyl acetate copolymers and their copolymers with carbon monoxide or ethylene/acrylic acid copolymers and their salts (anomers) as well as terpolymers of ethylene with propylene and a diene such as hexadiene, dicyclopentadiene or ethylidene-norbornene, and mixtures of such copolymers with one another and with polymers mentioned in 1) above, for example polypropylene/ethylene-propylene copolymers, LDPE/ethylene-vinyl acetate copolymers (EVA), LDPE/ethylene-acrylic acid copolymers (EAA), LLDPE/EVA, LLDPE/EAA and alternating or random polyalkylene/carbon monoxide copolymers and mixtures thereof with other polymers, for example polysiloxanes.

[0073] 4. Hydrocarbon resins (for example C_5 - C_{10}) including hydrogenated modifications thereof (e.g. tackifiers) and mixtures of polyalkylenes and starch.

[0074] 5. Polystyrene, poly(p-methylstyrene), poly(α -methylstyrene).

[0075] 6. Copolymers of styrene or α -methylstyrene with dienes or acrylic derivatives, for example styrene/butadiene, styrene/acrylonitrile, styrene/alkyl methacrylate, styrene/butadiene/alkyl methacrylate, styrene/maleic anhydride, styrene/acrylonitrile/methyl acrylate, mixtures of high impact strength of styrene copolymers and another polymer, for example a polyacrylate, a diene polymer or an ethylene/propylene/diene terpolymer, and block copolymers of styrene such as styrene/butadiene/styrene, styrene/isoprene/styrene, styrene/ethylene/butylene/styrene or styrene/ethylene/propylene/styrene.

[0076] 7. Graft copolymers of styrene or α -methylstyrene, for example styrene on polybutadiene, styrene on polybutadiene-styrene or polybutadiene-acrylonitrile copolymers; styrene and acrylonitrile (or methacrylonitrile) on polybutadiene, styrene, acrylonitrile and methyl methacrylate on polybutadiene, styrene and maleic anhydride on polybutadiene; styrene, acrylonitrile and maleic anhydride or maleimide on polybutadiene; styrene and maleimide on polybutadiene; styrene and alkyl acrylates or methacrylates on

polybutadiene; styrene and acrylonitrile on ethylene/propylene/diene terpolymers; styrene and acrylonitrile on polyalkyl acrylates or polyalkyl methacrylates, styrene and acrylonitrile on acrylate/butadiene copolymers, as well as mixtures thereof with the copolymers listed under 6), for example the copolymer mixtures known as ABS, MBS, ASA or AES polymers.

[0077] 8. Halogen-containing polymers such as polychloroprene, chlorinated rubbers, chlorinated and brominated copolymer of isobutylene-isoprene (halobutyl rubber), chlorinated or sulfochlorinated polyethylene, copolymers of ethylene and chlorinated ethylene, epichlorohydrin homo- and copolymers, especially polymers of halogen-containing vinyl compounds, for example polyvinyl chloride, polyvinylidene chloride, polyvinyl fluoride, polyvinylidene fluoride, as well as copolymers thereof such as vinyl chloroethylvinylidene chloride, vinyl chloride/vinyl acetate or vinylidene chloride/vinyl acetate copolymers.

[0078] 9. Polymers derived from α,β -unsaturated acids and derivatives thereof such as polyacrylates and polymethacrylates, polymethyl methacrylates, polyacrylamides and polyacrylonitriles, impact-modified with butyl acrylate.

[0079] 10. Copolymers of the monomers mentioned under 9) with each other or with other unsaturated monomers, for example acrylonitrile/butadiene copolymers, acrylonitrile/alkyl acrylate copolymers, acrylonitrile/alkoxyalkyl acrylate or acrylonitrile/vinyl halide copolymers or acrylonitrile/alkyl methacrylate/butadiene terpolymers.

[0080] 11. Polymers derived from unsaturated alcohols and amines or the acyl derivatives or acetals thereof, for example polyvinyl alcohol, polyvinyl acetate, polyvinyl stearate, polyvinyl benzoate, polyvinyl maleate, polyvinyl butyral, polyallyl phthalate or polyallyl melamine, as well as their copolymers with olefins mentioned in 1) above.

[0081] 12. Homopolymers and copolymers of cyclic ethers such as polyalkylene glycols, polyethylene oxide, polypropylene oxide or copolymers thereof with bisglycidyl ethers.

[0082] 13. Polyacetals such as polyoxymethylene and those polyoxymethylenes which contain ethylene oxide as a comonomer, polyacetals modified with thermoplastic polyurethanes, acrylates or MBS.

[0083] 14. Polyphenylene oxides and sulfides, and mixtures of polyphenylene oxides with styrene polymers or polyamides.

[0084] 15. Polyurethanes derived from hydroxyl-terminated polyethers, polyesters or polybutadienes on the one hand and aliphatic or aromatic polyisocyanates on the other, as well as precursors thereof.

[0085] 16. Polyamides and copolyamides derived from diamines and dicarboxylic acids and/or from aminocarboxylic acids or the corresponding lactams, for example polyamide 4, polyamide 6, polyamide 6/6, 6/10, 6/9, 6/12, 4/6, 12/12, polyamide 11, polyamide 12, aromatic polyamides starting from m-xylylene diamine and adipic acid; polyamides prepared from hexamethylenediamine and isophthalic or/and terephthalic acid and with or without an elastomer as modifier, for example poly-2,4,4'-trimethylhexamethylene terephthalamide or poly-m-phenylene isophthalamide; and also block copolymers of the aforementioned polyamides

US 2002/0120042 A1

Aug. 29, 2002

9

with polyolefins, olefin copolymers, ionomers or chemically bonded or grafted elastomers, or with polyethers, e.g. with polyethylene glycol, polypropylene glycol or polytetramethylene glycol, as well as polyamides or copolyamides modified with EPDM or ABS, and polyamides condensed during processing (RIM polyamide systems)

[0086] 17. Polyureas, polyimides, polyamide-imides, polyetherimides, polyesterimides, polyhydantoins and polybenzimidazoles.

[0087] 18. Polyesters derived from dicarboxylic acids and diols and/or from hydroxycarboxylic acids or the corresponding lactones, for example polyethylene terephthalate, polybutylene terephthalate, poly-1,4-dimethylolcyclohexane terephthalate and polyhydroxybenzoates, as well as block copolyester esters derived from hydroxyl-terminated polyethers, and also polyesters modified with polycarbonates or MBS.

[0088] 19. Polycarbonates and polyester carbonates

[0089] 20. Polysulfones, polyether sulfones and polyether ketones

[0090] 21. Crosslinked polymers derived from aldehydes on the one hand and phenols, ureas and melamines on the other hand, such as phenol/formaldehyde resins, urea/formaldehyde resins and melamine/formaldehyde resins

[0091] 22. Drying and non-drying alkyl resins.

[0092] 23. Unsaturated polyester resins derived from copolyesters of saturated and unsaturated dicarboxylic acids with polyhydric alcohols and vinyl compounds as crosslinking agents, and also halogen-containing modifications thereof of low flammability

[0093] 24. Crosslinkable acrylic resins derived from substituted acrylates, for example epoxy acrylates, urethane acrylates or polyester acrylates

[0094] 25. Alkyd resins, polyester resins and acrylate resins crosslinked with melamine resins, urea resins, isocyanates, isocyanurates, polyisocyanates or epoxy resins

[0095] 26. Crosslinked epoxy resins derived from aliphatic, cycloaliphatic, heterocyclic or aromatic glycidyl compounds, e.g. products of diglycidyl ethers of bisphenol A and bisphenol F, which are crosslinked with customary hardeners such as anhydrides or amines, with or without accelerators.

[0096] 27. Natural polymers such as cellulose, rubber, gelatin and chemically modified homologous derivatives thereof, for example cellulose acetates, cellulose propionates and cellulose butyrates, or the cellulose ethers such as methyl cellulose, as well as rosin and their derivatives.

[0097] 28. Blends of the aforementioned polymers (polyblends), for example PP/EPDM, Polyamide/EPDM or ABS, PVC/EVA, PVC/ABS, PVC/MBS, PC/ABS, PBI/ABS, PC/ASA, PC/PBT, PVC/CPE, PVC/acrylates, POM/thermoplastic PUR, PC/thermoplastic PUR, POM/acrylate, POM/MBS, PPO/III-PS, PPO/PA 6.6 and copolymers, PA/HDPE, PA/PP, PA/PPO, PBI/PC/ABS or PBT/PET/PC.

[0098] 29. Naturally occurring and synthetic organic materials which are pure monomeric compounds or mixtures of such compounds, for example mineral oils, animal and vegetable fats, oil and waxes, or oils, fats and waxes based

on synthetic esters (e.g. phthalates, adipates, phosphates or trimellitates) and also mixtures of synthetic esters with mineral oils in any weight ratios, typically those used as spinning compositions, as well as aqueous emulsions of such materials.

[0099] 30. Aqueous emulsions of natural or synthetic rubber, e.g. natural latex or latices of carboxylated styrene/butadiene copolymers.

[0100] The invention therefore furthermore relates to a composition comprising an organic material which is sensitive to oxidative, thermal or light-induced degradation and a novel stabilizer mixture.

[0101] The organic material is preferably a synthetic polymer, in particular from one of the above groups. Polyolefins are preferred, and polyethylene, polypropylene and copolymers thereof are particularly preferred.

[0102] The components of the novel stabilizer system can be added to the material to be stabilized either individually or mixed with one another. The components can be employed, independently of one another, in amounts of from 0.01 to 4.99%, with the proviso that the total amount of component a) and component b), c), d) or e) is from 0.02 to 5%, based on the total weight of the material to be stabilized.

[0103] The total amount of component a) and component b), c), d) or e) is preferably from 0.05 to 3%, in particular from 0.05 to 2%, or from 0.05 to 1%, based on the total weight of the material to be stabilized.

[0104] The weight ratio between component a) and component b), c), d) or e) is preferably from 20:1 to 1:20, in particular from 10:1 to 1:10, for example from 5:1 to 1:5.

[0105] The novel stabilizer mixture or the individual components thereof can be incorporated into the organic material by known methods, for example before or during shaping or by applying the dissolved or dispersed compounds to the organic material, if necessary with subsequent evaporation of the solvent. The individual components of the novel stabilizer mixture can be added to the materials to be stabilized in the form of a powder, granules or a masterbatch, which contains these components in, for example, a concentration of from 2.5 to 25% by weight.

[0106] If desired, the components of the novel stabilizer system can be melt blended with one another before incorporation in the organic material.

[0107] The novel stabilizer system or its components can be added before or during the polymerization or before the crosslinking.

[0108] The materials stabilized in this way can be used in a wide variety of forms, for example as films, fibres, tapes, moulding compositions, profiles or as binders for paints, adhesives or putties.

[0109] The stabilized organic materials of the invention may additionally also contain various conventional additives, for example:

[0110] 1. Antioxidants

[0111] 1.1. Alkylated monophenols, for example 2,6-di-tert-butyl-4-methylphenol, 2-tert-butyl-4,6-dimethylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,6-di-tert-butyl-4-n-butylphenol, 2,6-di-tert-butyl-4-isobutylphenol, 2,6-dicyclo-

US 2002/0120042 A1

10

Aug. 29, 2002

phenyl-4-methylphenol, 2-(α -methylcyclohexyl)-4,6-dimethylphenol, 2,6-di-octadecyl-4-methylphenol, 2,6-nonylcyclohexylphenol, 2,6-di-tert-butyl-4-methoxymethylphenol, nonylphenols which are linear or branched in the side chains, for example, 2,6-di-nonyl-4-methylphenol, 2,4-dimethyl-6-(1'-methylundec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methylheptadec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methylundec-1'-yl)phenol and mixtures thereof.

[0112] 1.2 Allylthiomethylphenols, for example 2,4-di-allylthiomethyl-6-tert-butylphenol, 2,4-di-allylthiomethyl-6-methylphenol, 2,4-di-allylthiomethyl-6-ethylphenol, 2,6-di-dodecylthiomethyl-4-nonylphenol.

[0113] 1.3. Hydroquinones and alkylated hydroquinones, for example 2,6-di-tert-butyl-1-methoxyphenol, 2,5-di-tert-butylhydroquinone, 2,5-di-tert-amylhydroquinone, 2,6-di-phenyl-4-octadecyloxyphenol, 2,6-di-tert-butylhydroquinone, 2,5-di-tert-butyl-1-hydroxy-4-nonylphenol, 3,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyphenylacetate, bis-(3,5-di-tert-butyl-4-hydroxyphenyl) adipate.

[0114] 1.4 Tocopherols, for example α -tocopherol, β -tocopherol, γ -tocopherol, δ -tocopherol and mixtures thereof (Vitamin E).

[0115] 1.5. Hydroxylated thiodiphenyl ethers, for example 2,2'-thiobis(6-tert-butyl-4-methylphenol), 2,2'-thiobis(4-octylphenol), 4,4'-thiobis(6-tert-butyl-3-methylphenol), 4,4'-thiobis(6-tert-butyl-2-methylphenol), 4,4'-thiobis(3,6-di-sec-amylphenol), 4,4'-bis-(2,6-dimethyl-4-hydroxyphenyl) disulfide.

[0116] 1.6 Alkylidenebisphenols, for example 2,2'-methylenebis(6-tert-butyl-4-methylphenol), 2,2'-methylenebis(6-tert-butyl-4-ethylphenol), 2,2'-methylenebis[4-methyl-6-(α -methylcyclohexyl)phenol], 2,2'-methylenebis[4-methyl-6-cyclohexylphenol], 2,2'-methylenebis[6-nonyl-4-methylphenol], 2,2'-methylenebis[4,6-di-tert-butylphenol], 2,2'-ethylenedis(6-tert-butyl-4-isobutylphenol), 2,2'-methylenebis[6-(α -methylbenzyl)-4-nonylphenol], 2,2'-methylenebis[6-(α -methylbenzyl)-4-nonylphenol], 4,4'-methylenebis(2,6-di-tert-butylphenol), 4,4'-methylenebis(6-tert-butyl-2-methylphenol), 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 2,6-bis(3-tert-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenol, 1,1,3-tris(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-3-n-dodecylmercaptobutane, ethylene glycol, bis[3,3-bis(3'-tert-butyl-4'-hydroxyphenyl)butyrate], bis[3-tert-butyl-4-hydroxy-5-methylphenyl]dicyclopentadiene, bis[2-(3'-tert-butyl-2'-hydroxy-5'-methylbenzyl)-6-tert-butyl-4-methylphenyl]terephthalate, 1,1-bis-(3,5-dimethyl-4-hydroxyphenyl)butane, 2,2-bis-(3,5-di-tert-butyl-4-hydroxyphenyl)propane, 2,2-bis-(5-tert-butyl-4-hydroxy-2-methylphenyl)-4-n-dodecylmercaptobutane, 1,1,5,5-tetra-(5-tert-butyl-4-hydroxy-2-methylphenyl)pentane.

[0117] 1.7. O-, N- and S-benzyl compounds, for example 3,5,5'-tri-tert-butyl-4,4'-dihydroxydibenzyl ether, octadecyl-4-hydroxy-3,5-dimethylbenzylmercaptacetate, tridecyl-4-hydroxy-3,5-di-tert-butylbenzylmercaptacetate, tris(3,5-di-tert-butyl-4-hydroxybenzyl)-amine, bis(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl) dithiosterephthalate, bis(3,5-di-tert-butyl-4-hydroxybenzyl)sulfide, isooctyl-3,5-di-tert-butyl-4-hydroxybenzylmercaptacetate.

[0118] 1.8 Hydroxybenzylated malonates, for example dioctadecyl-2,2'-bis-(3,5-di-tert-butyl-2-hydroxybenzyl)-

malonate, di-octadecyl-2-(3-tert-butyl-4-hydroxy-5-methylbenzyl)-malonate, di-dodecylmercaptobenzyl-2,2-bis-(3,5-di-tert-butylhydroxybenzyl)malonate, bis-[4-(1,1,3,3-tetra-methylbutyl)phenyl]-2,2-bis(3,5-di-tert-butylhydroxybenzyl)malonate.

[0119] 1.9 Aromatic hydroxybenzyl compounds, for example 1,3,5-tris-(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, 1,4-bis(3,5-di-tert-butyl-4-hydroxybenzyl)-2,3,5,6-tetramethylbenzene, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)phenol.

[0120] 1.10 Triazine Compounds, for example 2,4-bis(octylmercapto)-6-(3,5-di-tert-butyl-4-hydroxybenzyl)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxybenzyl)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxybenzyl)-1,3,5-triazine, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-1,2,3-triazine, 1,3,5-tris-(3,5-di-tert-butyl-4-hydroxybenzyl)isocyanurate, 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)isocyanurate, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenylethyl)-1,3,5-triazine, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)-hexahydro-1,3,5-triazine, 1,3,5-tris(3,5-dicyclohexyl-4-hydroxybenzyl)isocyanurate.

[0121] 1.11 Benzylphosphonates, for example dimethyl-2,5-di-tert-butyl-4-hydroxybenzylphosphonate, diethyl-3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl-3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl-5-tert-butyl-4-hydroxy-3-methylbenzyl-phosphonate, the calcium salt of the monoethyl ester of 3,5-di-tert-butyl-4-hydroxybenzyl-phosphonic acid.

[0122] 1.12. Arylamino-phenols, for example 4-hydroxy-lauramide, 4-hydroxystearamide, octyl N-(3,5-di-tert-butyl-4-hydroxyphenyl)carbamate.

[0123] 1.13. Esters of β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, n-octanol, i-octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethyl-hexanediol, trimethylpropane, 4-hydroxymethyl-1-phospho-2,6,7-trioxabicyclo[2.2.2]octane.

[0124] 1.14 Esters of β -(5-tert-butyl-4-hydroxy-3-methylphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, octanol, i-octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethyl-hexanediol, trimethylpropane, 4-hydroxymethyl-1-phospho-2,6,7-trioxabicyclo[2.2.2]octane.

[0125] 1.15. Esters of β -(3,5-dicyclohexyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, octanol, i-octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl)isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylpropane, 4-hydroxymethyl-1-phospho-2,6,7-trioxabicyclo[2.2.2]octane.

Aug. 29, 2002

[0126] 116. Esters of 3,5-di-*tert*-butyl-4-hydroxybenzoic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, methylene glycol, pentae-ythritol, tri-(hydroxyethyl)isocyanurate, *N,N*-bis-(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thia-pentadecanol, isomethylhexanediol, tri-methylpropa-ae-4-hydroxymethyl-1-phospha-2,6,7-trioxapicyclo[2.2.2]oc-tane

[0127] 1.17. Amides of β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionyl acid e.g. N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenyl)propionylhexamethylenediamine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenyl)propionyltrimethylendodiamine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenyl)propionylhydrazine

[0129] 1.19. Amino antioxidants, for example N,N-diisopropyl-p-phenylenediamine, N,N-di-*tert*-butyl-p-phenylenediamine, N,N-bis(1,4-dimethylphenyl)-p-phenylenediamine, N,N-bis(1-ethyl-3-methylphenyl)-p-phenylenediamine, N,N-bis(1-methylphenyl)-p-phenylenediamine, N,N-dicyclohexyl-p-phenylenediamine, N,N-diphenyl-p-phenylenediamine, N,N-bis(2-naphthyl)-p-phenylenediamine, N-isopropyl-N'-phenyl-p-phenylenediamine, N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine, N-(1-methylphenyl)-N'-phenyl-p-phenylenediamine, N-cyclohexyl-N'-phenyl-p-phenylenediamine, 4-(p-toluenesulfonyl)-diphenylamine, N,N-dimethyl-N,N-di-*sec*-butyl-p-phenylenediamine, diphenylamine, N-allyldiphenylamine, 4-isopropoxydiphenylamine, N-phenyl-1-naphthylamine, N-(4-*tert*-octylphenyl)-1-naphthylamine, N-phenyl-2-naphthylamine, octylated diphenylamine, for example p,p'-di-*tert*-octyldiphenylamine, 4-n-butylaminophenol, 4-butyrylamino-phenol, 4-nonamylamino-phenol, 4-dodecanoylamino-phenol, 1-octadecanylaminophenol, bis(4-methoxyphenyl)amine, 2,6-di-*tert*-butyl-4-methylaminomethylphenol, 2,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane, N,N,N',N'-tetramethyl-4,4'-diaminodiphenylmethane, 1,2-bis[(2-methylphenyl)amino]ethane, 1,2-bis(phenylamino)propane, (o-tolyl)biguanide, Bis[4-(1,3-dimethylbutyl)phenyl]amine, *tert*-octylated N-phenyl-1-naphthylamine, a mixture of mono- and dialkylated *tert*-butyl/*tert*-octyldiphenylamines, a mixture of mono- and dialkylated nonyldiphenylamines, a mixture of mono- and dialkylated dodecyldiphenylamines, a mixture of mono- and dialkylated isopropyldiphenylamines, a mixture of mono- and dialkylated *tert*-butyldiphenylamines, 2,3-dihydro-3,3-dimethyl-4H-1,4-dioxazine, phenothiazine, a mixture of mono- and dialkylated *tert*-butyl/*tert*-nonylphenothiazines, a mixture of mono- and dialkylated *tert*-octylphenothiazines, N-allylphenothiazine, N,N,N'-tetraphenyl-1,4-diaminobut-2-ene, N,N-bis(2,2,6,6-tetramethylpiperid-4-yl)-N-methylenediamine, bis(2,2,6,6-tetramethylpiperid-4-yl)isobutate, 2,2,6,6-tetramethylpiperidin-4-one, 2,2,6,6-tetramethylpiperidin-4-ol

[0131] 2.1 2-(2'-Hydroxyphenyl)benzotriazoles, for example 2-(2'-hydroxy-5-methylphenyl)-benzotriazole, 2-(3,5-di-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(5-tert-butyl-1,2'-hydroxyphenyl)benzotriazole, 2-(2'-hydroxy-5-(1,1,3,3-tetra-methylbutyl)phenyl)benzotriazole, 2-(3,5-

di-tert-butyl-2'-hydroxyphenyl]-5-chloro-benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-methoxyphenyl)-5-chloro-benzotriazole, 2-(3'-tert-butyl-5'-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(2'-hydroxy-4'-oxycyclohexenyl)benzotriazole, 2-(3',5'-di-tert-amyl-2'-hydroxyphenyl)benzotriazole, 2-(3',5'-bis-(α,α -dimethylbenzyl)-2'-hydroxyphenyl)benzotriazole, mixture of 2-(3'-tert-butyl-2'-hydroxy-5'-(2-octyloxy-carbonylphenyl)phenyl)-5-chloro-benzotriazole, 2-(3'-tert-butyl-5'-[2-(2-ethylhexyloxy)-carbonyl-ethyl]-2'-hydroxyphenyl)-5-chloro-benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-methoxycarbonyl-ethyl)phenyl)-5-chloro-benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-methoxycarbonyl-ethyl)phenyl)benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-octyloxy-carbonyl-ethyl)phenyl)benzotriazole, 2-(3'-tert-butyl-5'-[2-(2-ethylhexyloxy)-carbonyl-ethyl]-2'-hydroxyphenyl)benzotriazole, 2-(3'-dodecyl-2'-hydroxy-5'-methoxyphenyl)benzotriazole, and 2-(3'-tert-butyl-2'-hydroxy-5'-(2-octyloxy-carbonyl-ethyl)phenyl)benzotriazole, 2,2'-methylene-bis[4(1,1,3,3-tetramethylbutyl)-6-benzotriazole-2'-vinylphenyl], the transesterification product of 2-(3'-tert-butyl-5'-(2-methoxycarbonyl-ethyl)-2'-hydroxyphenyl)-2H-benzotriazole with polyethylene glycol 300; $[R-CH_2CH_2-COO(CH_2)_n]$, where R=3'-tert-butyl-4'-hydroxy-5'-2H-benzotriazole-2'-vinylphenyl.

[0133] 2.3. Esters of substituted and unsubstituted benzoic acids, as for example 4-tert-butylphenyl salicylate, phenyl salicylate, octylphenyl salicylate, dibenzoyl resorcinol, bis(4-tert-butylbenzoyl) resorcinol, benzoyl resorcinol, 2,4-di-tert-butylphenyl 3,5-di-tert-butyl 4-hydroxybenzoate, hexadecyl 3,5-di-tert-butyl-4-hydroxybenzoate, octadecyl 3,5-di-tert-butyl 4-hydroxybenzoate, 2-methyl-4,6-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate.

[0134] 24 Acrylates, for example ethyl α -cyano- β , β -diphenylacrylate, isooctyl α -cyano- β , β -diphenylacrylate, methyl α -carbomethoxycinnamate, methyl α -cyano- β -methoxy-p-methoxy-cinnamate, butyl α -cyano- β -methyl-p-methoxycinnamate, methyl α -carbomethoxy-p-methoxycinnamate and N-(β -carbomethoxy- β -cyano vinyl)-2-methylindoline

[0135] 2.5. Nickel compounds, for example nickel complexes of 2,2'-thiobis[4-(1,1,3,3-tetramethylbutyl)phenol], such as the 1:1 or 1:2 complex, with or without additional ligands such as n-butylamine, triethanolamine or N-cyclohexylethanolamine, nickel dibutylthiocarbamate, nickel salts of the monoalkyl esters, e.g. the methyl or ethyl ester, of 4-hydroxy-3,5-di-*n*-butylbenzylphosphonic acid, nickel complexes of hexamines, e.g. of 2-hydroxy-4-methylphenyl undecylketoxime, nickel complexes of 1-phenyl-4-tolyl-5-hydroxypyrazole, with or without additional ligands

[0136] 2° Sterically hindered amines, for example bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate, bis(2,2,6,6-tetramethyl-4-piperidyl)succinate, bis(1,2,2,6,6-pentamethyl-4-piperidyl)sebacate, bis(1-octyloxy-2,2,6,6-tetramethyl-4-piperidyl)sebacate, bis(1,2,2,5,6-pentamethyl-4-piperidyl) n-butyl-3,5-di-tert-butyl-4-hydroxybenzylmalonate, the condensate of 1-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid, the condensate of N,N'-

US 2002/0120042 A1

Aug. 29, 2002

12

bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-tert-octyl amino-2,6-dichloro-1,3,5-triazine, tris(2,2,6,6-tetramethyl-4-piperidyl)dimethylsulfate, tetrakis(2,2,6,6-tetramethyl-4-piperidyl)-1,2,3,4-butanetetracarboxylate, 1,1'-(1,2-ethanediyl)bis(3,3,5,5-tetramethylpiperazinone), 4-benzoyl-2,2,6,6-tetramethylpiperidine, 4-stearoyloxy-2,2,6,6-tetramethylpiperidine, bis(1,2,2,6,6-pentamethylpiperidyl)-2-n-butyl-2-(2-hydroxy-3,5-di-tert-butylbenzyl)malonate, 3-n-octyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decan-2,4-dione bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl)succinate, bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl)succinate, the condensate of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-morpholino-2,6-dichloro-1,3,5-triazine, the condensate of 2-chloro-4,6-bis(4-n-butylamino-2,2,6,6-tetramethylpiperidyl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane, the condensate of 2-chloro-4,6-di-(4-n-butylamino-1,2,2,6,6-pentamethylpiperidyl)-1,3,5-triazine and 1,2-bis-(3-aminopropylamino)ethane, 8-acetyl-3-dodecyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decan-2,4-dione, 3-dodecyl-1-(2,2,6,6-tetramethyl-4-piperidyl)pyrrolidine-2,5-dione, 3-dodecyl-1-(1,2,2,6,6-pentamethyl-4-piperidyl)pyrrolidine-2,5-dione, a mixture of 4-hexadecyloxy- and 4-stearoyloxy-2,2,6,6-tetramethylpiperidine, a condensation product of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-cyclohexylamino-2,6-dichloro-1,3,5-triazine, a condensation product of 1,2-bis(3-aminopropylamino)ethane and 2,4,6-trichloro-1,3,5-triazine as well as 4-butylamino-2,2,6,6-tetramethylpiperidine (CAS Reg. No. [136504-96-6]), N-(2,2,6,6-tetramethyl-4-piperidyl)-n-dodecylsuccinimide, N-(1,2,2,6,6-pentamethyl-4-piperidyl)-n-dodecylsuccinimide, 2-undecyl-7,7,9,9-tetramethyl-1-oxa-3,8-diaza-4-oxo-spiro[4.5]decan-2,4-dione, a reaction product of 7,7,9,9-tetramethyl-2-cyclo-undecyl-1-oxa-3,8-diaza-4-oxospiro[4.5]decan-2,4-dione and epichlorohydrin.

[0137] 2.7. Oxamides, for example 4,4'-diethyloxyoxanilide, 2,2'-diethyloxyoxanilide, 2,2'-diethyloxy-5,5'-di-tert-butyl-oxanilide, 2-ethoxy-2'-ethyloxyoxanilide, N,N'-bis(3-dimethylaminopropyl)oxamide, 2-ethoxy-5-tert-butyl-2'-ethoxyoxanilide and its mixture with 2-ethoxy-2'-ethyl-5,4-di-tert-butyl-oxanilide and mixtures of or- and para-methoxy-disubstituted oxanilides and mixtures of o- and p-ethoxy-disubstituted oxanilides.

[0138] 2.8. 2-(2-Hydroxyphenyl)-1,3,5-triazines, for example 2,4,6 tris(2-hydroxy-4-octyloxyphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2,4-dihydroxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2,4-bis(2-hydroxy-4-propyloxyphenyl)-6-(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(4-methylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-dodecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-undecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-butyloxy-propoxy)phenyl]-4,6-bis(2,4-dimethyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-octyloxy-propoxy)phenyl]-4,6-bis(2,4-dimethyl)-1,3,5-triazine, 2-[4-(dodecyloxy)tridecyloxy-2-hydroxypropoxy]-2-hydroxy-phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-dodecyloxy-propoxy)phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-hexyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-methoxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2,4,6-tris(2-hy-

droxy-4-(3-butoxy-2-hydroxy-propoxy)phenyl)-1,3,5-triazine, 2-(2-hydroxyphenyl)-4-(4-methoxyphenyl)-6-phenyl-1,3,5-triazine.

[0139] 3. Metal deactivators, for example N,N'-diphenyloxamide, N-salicyl-N'-salicyloyl hydrazine, N,N'-bis(salicyloyl) hydrazine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl) hydrazine, 3-salicyloylamino-1,2,4-triazole, bis(benzylidene)oxalyl dihydrazide, oxanilide, isophthaloyl dihydrazide, sebacoyl bisphenylhydrazide, N,N'-di-acetyladi-poyl dihydrazide, N,N'-bis(salicyloyl)oxalyl dihydrazide, N,N'-bis(salicyloyl)-thiopropionyl dihydrazide.

[0140] 4. Phosphites and phosphonites, for example triphenyl phosphite, diphenyl alkyl phosphites, phenyl dialkyl phosphites, tri(nonylphenyl) phosphite, tri-lauryl phosphite, tri-octadecyl phosphite, distearyl pentacerythritol diphosphite, tris(2,4-di-tert-butylphenyl) phosphite, diisodecyl pentacerythritol diphosphite, bis(2,4-di-tert-butylphenyl) pentacerythritol diphosphite, bis(2,6-di-tert-butyl-4-methylphenyl)-pentacerythritol diphosphite, diisodecylhexapentaerythritol diphosphite, bis(2,4-di-tert-butyl-6-methylphenyl) pentacerythritol diphosphite, bis(2,4,6-tris(tert-butylphenyl) pentacerythritol diphosphite, tris(aryl sorbitol triphosphite, tetrakis(2,4-di-tert-butylphenyl) 4,4'-biphenylene diphosphonite, 6-undecyl-oxy-2,4,8,10-tetra-tert-butyl-12H-dibenzo[d,g]-1,3,2-dioxaphosphocin, 6-fluoro-2,4,8,10-tetra-tert-butyl-12-methyl-dibenzo[d,g]-1,3,2-dioxaphosphocin, bis(2,4-di-tert-butyl-6-methylphenyl)methylphosphite, bis(2,4-di-tert-butyl-6-methylphenyl)ethylphosphite.

[0141] 5. Hydroxylamines, for example, N,N-dibenzylhydroxylamine, N,N-diethylhydroxylamine, N,N-diethylhydroxylamine, N,N-dilaurylhydroxylamine, N,N-dihexadecylhydroxylamine, N,N-dioctadecylhydroxylamine, N-hexadecyl-N-octadecylhydroxylamine, N-heptadecyl-N-octadecylhydroxylamine, N,N-dialkylhydroxylamine derived from hydrogenated tallow amine.

[0142] 6. Nitrones, for example, N-benzyl-alpha-phenyl-nitron, N-ethyl-alpha-methyl-nitron, N-octyl-alpha-heptyl-nitron, N-lauryl-alpha-undecyl-nitron, N-tetradecyl-alpha-tridecyl-nitron, N-hexadecyl-alpha-pentadecyl-nitron, N-octadecyl-alpha-heptadecyl-nitron, N-hexadecyl-alpha-heptadecyl-nitron, N-octadecyl-alpha-pentadecyl-nitron, N-heptadecyl-alpha-heptadecyl-nitron, N-octadecyl-alpha-hexadecyl-nitron, nitron derived from N,N-dialkylhydroxylamine derived from hydrogenated tallow amine.

[0143] 7. Thioetherobis, for example, dilauryl thiopropionate or distearyl thiopropionate.

[0144] 8. Peroxide scavengers, for example esters of beta-thiodipropionic acid, for example the lauryl, stearyl, myristyl or undecyl esters, mercapto-benzimidazole or the zinc salt of 2-mercapto-benzimidazole, zinc dibutylthiocarbamate, dodecyl disulfide, pentacerythritol tetrakis(beta-dodecylmercapto)propionate.

US 2002/0120042 A1

Aug. 29, 2002

13

[0145] 9. Poly amide stabilizers, for example, copper salts in combination with iodides and/or phosphorus compounds and salts of divalent manganese.

[0146] 10. Basic co-stabilizers, for example, melamine, polyvinylpyrrolidone, dicyandiamide, triallyl cyanurate, urea derivatives, hydrazine derivatives, amines, polyamides, polyurethanes, alkali metal salts and alkaline earth metal salts of higher fatty acids for example calcium stearate, zinc stearate, magnesium benzoate, magnesium stearate, sodium ricinoleate and potassium palmitate, antimony pyrocatecholate or tin pyrocatecholate.

[0147] 11. Nucleating agents, for example, inorganic substances such as talcum, metal oxides such as titanium dioxide or magnesium oxide, phosphates, carbonates or sulfates of, preferably, alkaline earth metals; organic compounds such as mono- or polycarboxylic acids and the salts thereof, e.g. 4-tert-butylbenzoic acid, adipic acid, diphenylacetic acid, sodium succinate or sodium benzoate, polymeric compounds such as ionic copolymers ("ionomers").

[0148] 12. Fillers and reinforcing agents, for example, calcium carbonate, silicates, glass fibres, glass pulbs, asbestos, talc, kaolin, mica, barium sulfate, metal oxides and hydroxides, carbon black, graphite, wood flour and flours or fibers of other natural products, synthetic fibers.

[0149] 13. Other additives, for example, plasticizers, lubricants, emulsifiers, pigments, rheology additives, catalysts, flow-control agents, optical brighteners, flameproofing agents, antistatic agents and blowing agents.

[0150] 14. Benzofuranones and indenones, for example those disclosed in U.S. Pat. No. 4,325,863, U.S. Pat. No. 3,382,244, U.S. Pat. No. 5,175,312, U.S. Pat. No. 5,216,052, U.S. Pat. No. 5,252,543, DE-A-4 316 611, DE-AA 316 622, DE-A4 316 876, EP-A-0 589 839 or EP-A-0 591 102 or 3-[4-(2-acetoxyethoxy)phenyl]-5,7-di-tert-butyl-benzofuran-2-one, 5,7-di-tert-butyl-3-[4-(2-sisapoyloxyethoxy)phenyl]benzofuran-2-one, 3,3'-bis[5,7-di-tert-butyl-3-[4-(2-hydroxyethoxy)phenyl]benzofuran-2-one], 5,7-di-tert-butyl-3-[4-(ethoxyphenyl)benzofuran-2-one], 3-(4-acetoxy-3,5-dimethylphenyl)-5,7-di-tert-butyl-benzofuran-2-one, 3-(3,5-dimethyl-4-pivaloyloxyphenyl)-5,7-di-tert-butyl-benzofuran-2-one.

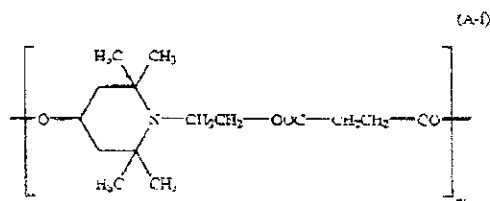
[0151] The weight ratio between the novel stabilizer mixture and the conventional additives can be, for example, from 1:0.5 to 1:5.

[0152] The invention furthermore relates to the use of the novel stabilizer mixture for stabilizing organic material against oxidative, thermal or light-induced degradation.

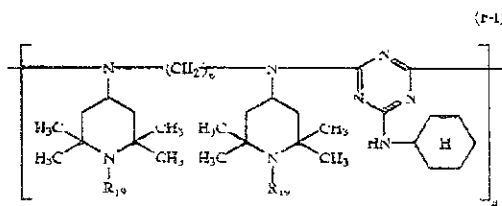
[0153] The organic materials stabilized by means of the novel stabilizer system are distinguished not only by significantly improved light stability, but also in some cases by improved thermal stability.

[0154] The foregoing also applies correspondingly to the following stabilizer mixture, which is likewise a subject-matter of the present invention:

[0155] A stabilizer mixture comprising a compound of the formula A-I



[0156] in which n, is a number from 2 to 25, in particular from 2 to 15, and a compound of the formula F-I



[0157] in which R₁₀ is hydrogen, C₁-C₆alkyl, O, —CH₂CN, C₅-C₆alkenyl, C₇-C₈phenylalkyl, C₇-C₈phenylalkyl which is substituted by C₁-C₄alkyl on the phenyl radical, or C₁-C₆acyl, and n₁ is a number from 2 to 25, in particular from 2 to 10.

[0158] R₁₀ is preferably hydrogen or C₁-C₄alkyl, in particular hydrogen.

[0159] The individual components of this stabilizer mixture are known and are in some cases commercially available. They can furthermore also be prepared analogously to the processes described in U.S. Pat. No. 4,233,412 and U.S. Pat. No. 4,086,204.

[0160] A stabilizer mixture comprising @TINU VIN 622 and @DASTIB 1082 is preferred.

[0161] The meanings of the terminal groups which saturate the free valences in the compounds of the formulae A-I and F-I are dependent on the processes used for their preparation.

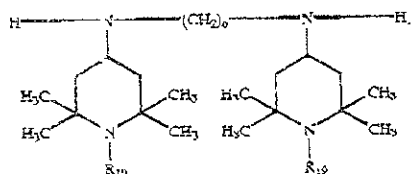
[0162] The terminal groups can also be modified after the preparation of the compounds.

[0163] The comments made regarding the terminal groups of the compounds of the formula I apply correspondingly to the terminal groups of the compound of the formula A-I.

[0164] If the compound of the formula F-I is prepared by reacting a compound of the formula

Aug. 29, 2002

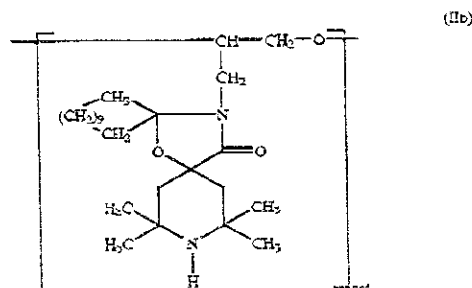
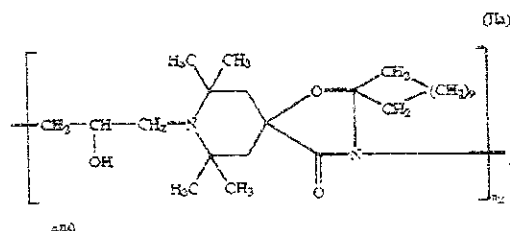
[0165] in which X is, for example, halogen, in particular chlorine, with a compound of the formula

Xc1nc(NC2CCCCC2)nc1
$$\begin{array}{c} \text{---} \text{N}^+ \text{---} (\text{CH}_2)_n \text{---} \text{N}^+ \text{---} \text{H} \\ | \qquad \qquad \qquad | \\ \text{C}_6\text{H}_4 \qquad \qquad \text{C}_6\text{H}_4 \\ | \qquad \qquad \qquad | \\ \text{C} \qquad \qquad \text{C} \\ / \quad \backslash \quad / \quad \backslash \\ \text{H}_3\text{C} \quad \text{CH}_3 \quad \text{H}_3\text{C} \quad \text{CH}_3 \\ | \qquad \qquad | \\ \text{H}_3\text{C} \qquad \text{CH}_3 \quad \text{H}_3\text{C} \quad \text{CH}_3 \\ | \qquad \qquad | \\ \text{R}_{10} \qquad \qquad \text{R}_{19} \end{array}$$
*C1CC(C)(C)N(R2)CC1

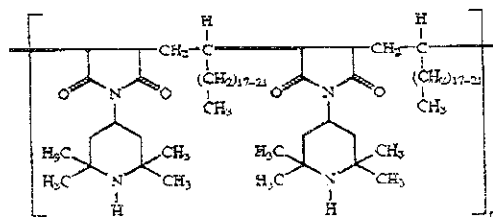
[0170] Light Stabilizers Used in Examples 1-4:

$$\left[\text{O} - \text{C}_6\text{H}_2(\text{CH}_3)_4 - \text{N} - \text{CH}_2\text{CH}_2 - \text{OOC} - \text{CH}_2\text{CH}_2 - \text{CO} \right]_n$$

[0173] Mixture of the compounds



[0175] Compound C-1:



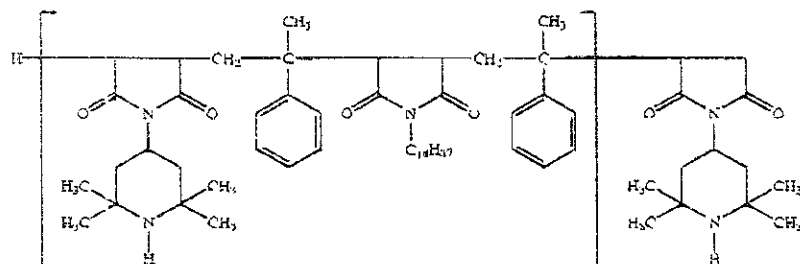
[0176] The mean value of α_j is 3.2.

US 2002/01:20042 A1

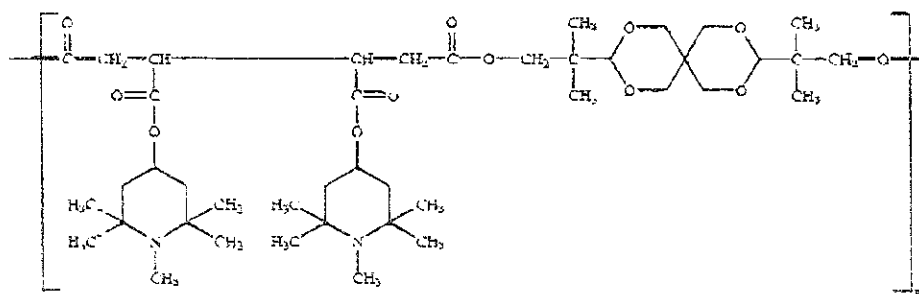
Aug. 29, 2002

15

[0177] Compound C-2:

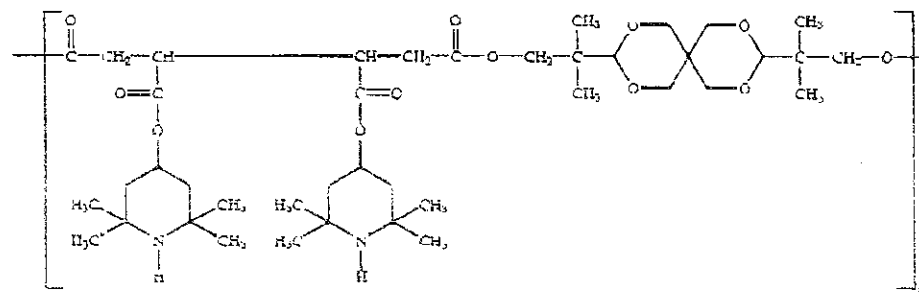


[0178] Compound D-1:



[0179] The mean value of n_1 is 2.5

[0180] Compound D-2



US 2002/0120042 A1

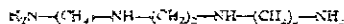
Aug. 29, 2002

16

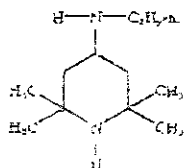
[0181] The mean value of n_g is 3.5

[0182] Compound E

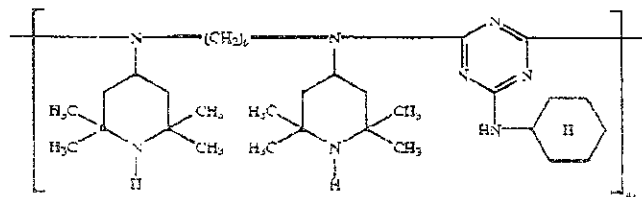
[0183] Product obtainable by reacting a product, obtained by reacting a pyrimidine of the formula



[0184] with cyanuric chloride, with a compound of the formula



[0185] Compound F



[0186] The mean value of n_g is 4.4.

EXAMPLE 1

Light Stabilization Action in Polypropylene Tapes

[0187] 100 parts of polypropylene powder [melt flow index 2.4 g/10 min (230° C., 2100 g)] are mixed in a tumble mixer with 0.05 part of pentaerythrityl tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], 0.05 part of tris(2,4-di-tert-butylphenyl) phosphite, 0.1 part of calcium stearate and the amount of light stabilizer indicated in Table 1, and the mixture is subsequently granulated in an extruder at a temperature of from 180 to 220° C.

[0188] The granules obtained are converted into a film in a second extruder fitted with a flat film die (temperature from 220 to 260° C.), and the film is cut into tapes, which are subsequently stretched in a ratio of 1:5.25 at elevated temperature and wound up (linear density of the tapes from 700 to 900 den; tear strength from 5.5 to 6.5 g/den).

[0189] The polypropylene tapes produced in this way are mounted without tensioned on sample carriers and weathered in a WEATHER-O-METER C105. After various times, 5 test specimens are taken in each case and their tear strength is determined. The measure used for the protective action of the individual light stabilizers is the exposure time before the tear strength of the tapes drops to 50% of the initial value. The values obtained are shown in Table 1.

TABLE 1

Light stabilizer	Hours in WEATHER-O-METER C105 to 50% of tear strength
None	550
0.1% of compound A	2540
0.1% of compound B	3050
0.05% of compound A and 0.05% of compound E	>3100

EXAMPLE 2

Light Stabilization Action in Polypropylene Tapes

[0190] Samples are produced analogously to the process described in Example 1. The tapes are stretched at a ratio of 1:5.25. The experimental results are shown in Table 2.

TABLE 2

Light stabilizer	Hours in WEATHER-O-METER C105 to 50% residual tear strength
None	570
Compound A	1730
Compound C-1	1900
Compound C-2	1250
Compound A and compound C-1 in a ratio of 1:1	2550
Compound A and compound C-2 in a ratio of 1:1	2000

EXAMPLE 3

Light Stabilization Action in Polypropylene Block Copolymer Films

[0191] 100 parts of polypropylene block copolymer powder are homogenized for 10 minutes at 200° C. in a Brabender plastograph with 0.05 part of pentaerythrityl tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], 0.10 part of tris(2,4-di-tert-butylphenyl) phosphite, 0.1 part of calcium stearate and the light stabilizers shown in Table 3. The composition obtained is removed from the compounder as rapidly as possible and pressed in a toggle press to give a

US 2002/0120042 A1

Aug. 29, 2002

17

sheet with a thickness of 2-3 mm. A piece of the resultant green pressing is cut out and pressed between two high-gloss hard aluminum foils for 6 minutes at 250° C. by means of a hydraulic bench press to give a sheet with a thickness of 0.5 mm, which is immediately cooled in a water-cooled press. Pieces, each measuring 60 mm×25 mm are then stamped out of this 0.5 mm sheet and exposed to light in a WEATHER-O-METER C1 65 (black panel temperature 63±2° C, no exposure to rain water). These test specimens are removed from the exposure apparatus at regular intervals and tested for their carbonyl content in an IR spectrometer. The increase in the carbonyl absorbance during exposure is a measure of the photooxidative degradation of the polymer and is known from experience to be associated with a deterioration in the mechanical properties. The results are shown in Table 3.

TABLE 3

Light stabilizer	Increase in WEATHER-O-METER C1 65 in 0.2 carbonyl absorbance
0.2% of compound A	2240
0.2% of compound B	1710
0.2% of compound C-1	303
0.2% of compound D	2400
0.2% of compound E	1550
0.2% of compound F and 0.1% of compound I	3360
0.1% of compound A and 0.1% of compound D-1	1540
0.1% of compound F and 0.1% of compound E	3330
0.1% of compound F and 0.1% of compound I	2660

EXAMPLE 4

Light Stabilization Action in High-density Polyethylene Films

[0192] 100 parts of high-density polyethylene powder (density=0.965 g/cm³) are homogenized for 10 minutes at 180° C. in a Brabender plastograph with 0.033 part of pentaerythrityl tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], 0.066 part of tris(2,4-di-tert-butylphenyl) phosphite, 0.1 part of calcium stearate and the light stabilizers shown in Table 4. The composition in the amounts obtained is removed from the compounder as rapidly as possible and pressed in a toggle press to give a sheet with a thickness of 2-3 mm. A piece of the resultant green pressing is cut out and pressed between two high-gloss hard aluminum foils for 6 minutes at 210° C. by means of a hydraulic bench press to give a sheet with a thickness of 0.5 mm, which is immediately cooled in a water-cooled press. Pieces measuring 60 mm×25 mm are then stamped out of this 0.5 mm sheet and exposed to light in a Weather-O-meter C1 65 (black panel temperature 63±2° C, no exposure to rain water). These test specimens are removed from the exposure apparatus at regular intervals and tested for their vinyl content in an IR spectrometer. The increase in the vinyl absorbance (909 cm⁻¹) during exposure is a measure of the photooxidative degradation of the polymer and is known from experience to be associated with a deterioration in the mechanical properties. The results are shown in Table 4.

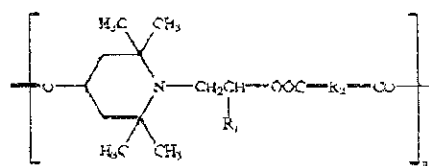
TABLE 4

Light stabilizer	Vinyl absorbance after 7222 hours in the WEATHER-O-METER C1 65
None	0.061
	after 336 hours
0.1% of compound A	0.039
0.1% of compound B	0.046
0.1% of compound C-1	0.058
0.1% of compound C-2	0.143
	after 5286 hours
0.1% of compound D-1	0.040
0.1% of compound D-2	0.040
0.1% of compound E	0.054
0.1% of compound F	0.051
0.05% of compound A and 0.05% of compound B	0.036
0.05% of compound A and 0.05% of compound C-1	0.033
0.05% of compound A and 0.05% of compound C-2	0.039
0.05% of compound A and 0.05% of compound D-1	0.037
0.05% of compound A and 0.05% of compound D-2	0.034
0.05% of compound A and 0.05% of compound E	0.037
0.05% of compound A and 0.05% of compound F	0.037

What is claimed is:

1. A stabilizer mixture comprising a component a) and a component b), c), d) or e), where

component a) is at least one compound of the formula I

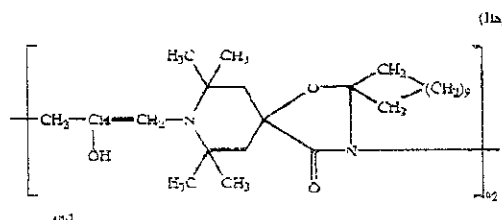


in which R₁ is hydrogen or methyl,

R₂ is a direct bond or C₁-C₁₀alkylene and

n₁ is a number from 2 to 50;

component b) is at least one compound of the formulae IIa and IIb

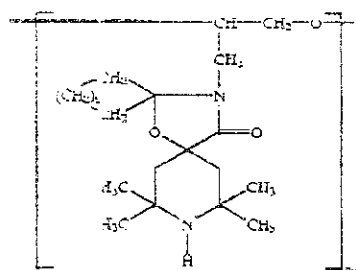


US 2002/0120042 A1

Aug. 29, 2002

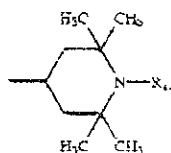
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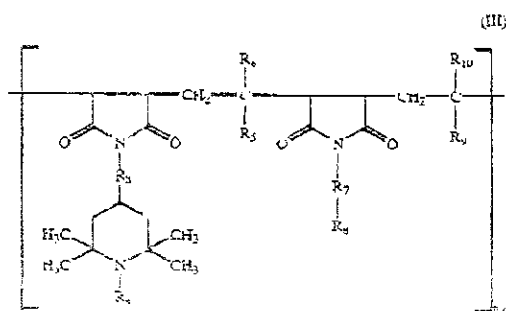
(IIIa)

in which R_3 and R_4 , independently of one another, are a direct bond or an $-N(X_1)-C(=O)-X_2-C(=O)-N(X_3)-$ group, where X_1 and X_3 , independently of one another, are hydrogen, C_1-C_{10} alkyl, C_3-C_{12} cycloalkyl, phenyl, C_7-C_{10} phenylalkyl or a group of the formula IV



(IV)

in which n_2 and n_3 are a number from 2 to 50,
 component c) is at least one compound of the formula III



(III)

and X_2 is a direct bond or C_1-C_{10} alkylene,

R_5 is hydrogen, C_1-C_{10} alkyl, O_2-CH_2CN , C_3-C_{10} alkenyl, C_7-C_{10} phenylalkyl,

C_7-C_{10} phenylalkyl which is substituted by C_1-C_{10} alkyl on the phenyl radical, or C_2-C_{10} acyl,

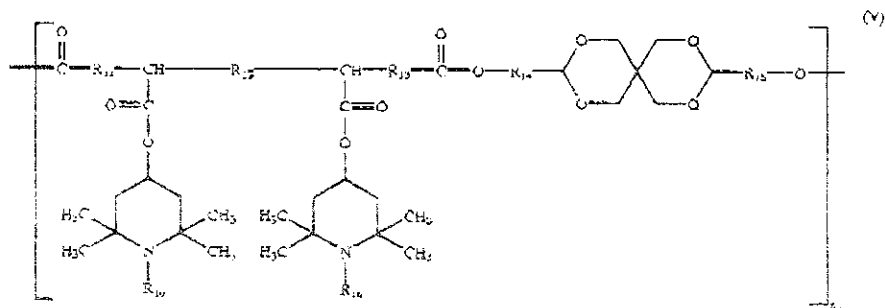
R_6 , R_7 , R_8 and R_{10} , independently of one another, are hydrogen, C_1-C_{10} alkyl,

C_3-C_{12} cycloalkyl or phenyl,

R_9 is hydrogen, C_1-C_{10} alkyl, C_3-C_{12} cycloalkyl, C_7-C_{10} phenylalkyl, phenyl or a group of the formula IV, and

n_3 is a number from 1 to 50;

component d) is at least one compound of the formula V



(V)

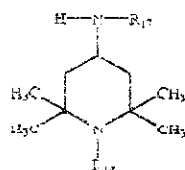
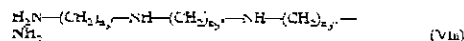
US 2002/0120042 A1

Aug. 29, 2002

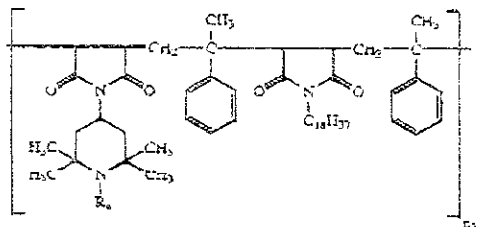
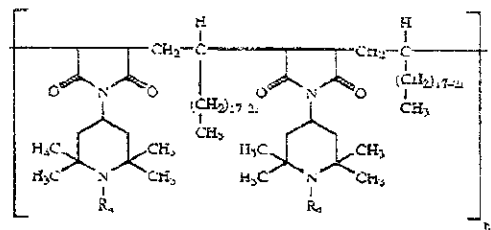
19

in which R_{11} , R_{12} , R_{13} , R_{14} , and R_{15} , independently of one another, are a direct bond or C_1 - C_{20} alkylene, R_{16} is as defined for R_{10} and n_4 is a number from 1 to 50; and

component w) is a product obtainable by reacting a product, obtained by reacting a polyamine of the formula VIa with cyanuric chloride, with a compound of the formula VIb



(VIb)

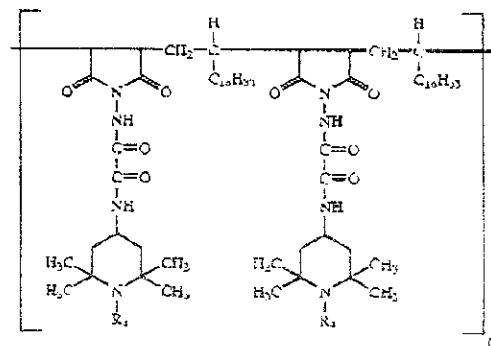


in which n_1 , n_2 , and n_3 , independently of one another, are a number from 2 to 12, R_{17} is hydrogen, C_1 - C_{12} alkyl, C_5 - C_{12} cycloalkyl, phenyl or C_7 - C_9 phenylalkyl, and R_{18} is as defined for R_6

2. A stabilizer mixture according to claim 1, in which R_1 is hydrogen, R_2 is ethylene and n_1 is a number from 2 to 25.

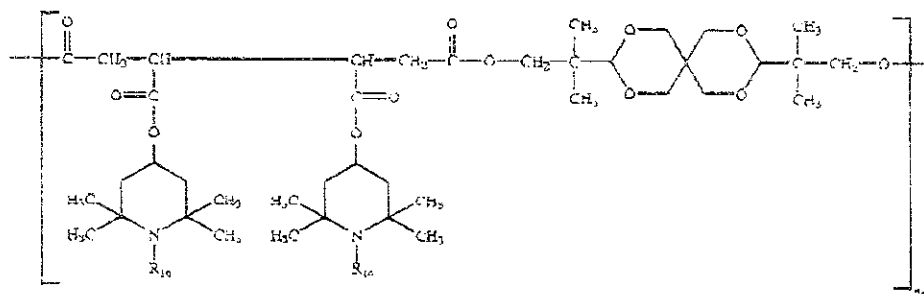
3. A stabilizer mixture according to claim 1, in which R_3 and R_7 are a direct bond or an $-N(X_1)-CO-X_2-CO-N(X_2)-$ group, where X_1 and X_2 , independently of one another, are hydrogen or C_1 - C_4 alkyl and X_3 is a direct bond, R_4 is hydrogen, C_1 - C_6 alkyl, OH, C_2 - C_{12} alkoxy, C_2 - C_6 cycloalkoxy, allyl, benzyl or acetyl, R_5 and R_6 are C_1 - C_{22} alkyl or phenyl, R_9 and R_{10} are hydrogen or C_1 - C_6 alkyl, R_{11} is C_1 - C_{25} alkyl or a group of the formula IV, R_{11} , R_{13} , R_{14} and R_{15} are C_1 - C_6 alkylene, R_{12} is a direct bond, and R_{13} is as defined for R_4 .

4. A stabilizer mixture according to claim 1, in which component c) is at least one compound of the formula



in which R_4 is hydrogen or methyl, and n_3 is a number from 1 to 50

5. A stabilizer mixture according to claim 1, in which component d) is at least one compound of the formula



US 2002/0: 20042 A1

20

Aug. 29, 2002

in which R_{16} is hydrogen or methyl, and n_4 is a number from 1 to 50

6. A stabilizer mixture according to claim 1, in which n_5 , n_6 and n_7 , independently of one another, are a number from 2 to 4, R_{17} is C_1 - C_4 alkyl, and R_{18} is hydrogen

7. A stabilizer mixture according to claim 1, which comprises components a) and b).

8. A stabilizer mixture according to claim 1, which comprises components a) and c).

9. A stabilizer mixture according to claim 1, which comprises components a) and d).

10. A stabilizer mixture according to claim 1, which comprises components a) and e).

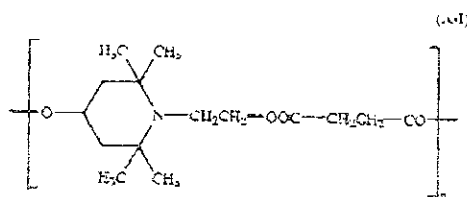
11. A composition comprising an organic material which is sensitive to oxidative, thermal or light-induced degradation and a stabilizer mixture according to claim 1

12. A composition according to claim 11, in which the organic material is a polyolefin

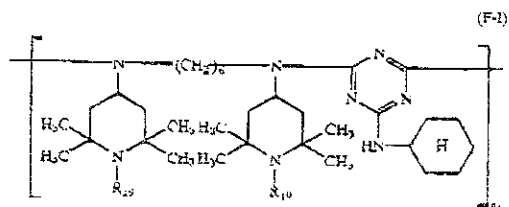
13. A composition according to claim 11, in which the organic material is polyethylene, polypropylene or a copolymer of polyethylene or polypropylene

14. A process for stabilizing an organic material which is sensitive to oxidative, thermal or light-induced degradation, which comprises incorporating a stabilizer mixture according to claim 1 into the organic material

15. A stabilizer mixture comprising a compound of the formula A-1,



in which n_1 is a number from 2 to 25, and a compound of the formula F-1,



in which R_{19} is hydrogen, C_1 - C_4 alkyl, O , $-CH_2CN$, C_3 - C_6 alkenyl, C_7 - C_6 phenylalkyl, C_7 - C_6 phenylalkyl which is substituted by C_1 - C_4 alkyl on the phenyl radical, or C_1 - C_6 acyl, and n_2 is a number from 2 to 25

* * * * *

JS 44 (Rev 11/04)

CIVIL COVER SHEET

The JS-44 civil cover sheet and the information contained herein neither replace nor supplement the filing and service of pleadings or other papers as required by law, except as provided by local rules of court. This form, approved by the Judicial Conference of the United States in September 1974, is required for the use of the Clerk of Court for the purpose of initiating the civil docket sheet. (SEE INSTRUCTIONS ON THE REVERSE OF THE FORM.)

I. (a) PLAINTIFFS Ciba Specialty Chemicals Corporation (b) County of Residence of First Listed Plaintiff <u>San Mateo County, CA</u> (EXCEPT IN U.S. PLAINTIFF CASES) (c) Attorney's (Firm Name, Address, and Telephone Number) Chad M. Shandler Richards, Layton & Finger One Rodney Square 920 North King Street Wilmington, DE 19801 302-651-7700	DEFENDANTS 3V, Inc. County of Residence of First Listed Defendant <u>New Castle County, DE</u> (IN U.S. PLAINTIFF CASES ONLY) NOTE: IN LAND CONDEMNATION CASES, USE THE LOCATION OF THE LAND INVOLVED Attorneys (If Known)
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II. BASIS OF JURISDICTION (Place an "X" in One Box Only) <input type="checkbox"/> 1 U.S. Government Plaintiff <input type="checkbox"/> 2 U.S. Government Defendant <input checked="" type="checkbox"/> 3 Federal Question (U.S. Government Not a Party) <input type="checkbox"/> 4 Diversity (Indicate Citizenship of Parties in Item III)	III. CITIZENSHIP OF PRINCIPAL PARTIES (Place an "X" in One Box for Plaintiff and One Box for Defendant) <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="text-align: left;">(For Diversity Cases Only)</th> <th style="text-align: center;">PTF</th> <th style="text-align: center;">DEF</th> <th style="text-align: left;"></th> <th style="text-align: center;">PTF</th> <th style="text-align: center;">DEF</th> </tr> <tr> <td>Citizen of This State</td> <td style="text-align: center;"><input type="checkbox"/> 1</td> <td style="text-align: center;"><input type="checkbox"/> 1</td> <td>Incorporated or Principal Place of Business In This State</td> <td style="text-align: center;"><input checked="" type="checkbox"/> 4</td> <td style="text-align: center;"><input checked="" type="checkbox"/> 4</td> </tr> <tr> <td>Citizen of Another State</td> <td style="text-align: center;"><input type="checkbox"/> 2</td> <td style="text-align: center;"><input type="checkbox"/> 2</td> <td>Incorporated and Principal Place of Business In Another State</td> <td style="text-align: center;"><input type="checkbox"/> 5</td> <td style="text-align: center;"><input type="checkbox"/> 5</td> </tr> <tr> <td>Citizen or Subject of a Foreign Country</td> <td style="text-align: center;"><input type="checkbox"/> 3</td> <td style="text-align: center;"><input type="checkbox"/> 3</td> <td>Foreign Nation</td> <td style="text-align: center;"><input type="checkbox"/> 6</td> <td style="text-align: center;"><input type="checkbox"/> 6</td> </tr> </table>	(For Diversity Cases Only)	PTF	DEF		PTF	DEF	Citizen of This State	<input type="checkbox"/> 1	<input type="checkbox"/> 1	Incorporated or Principal Place of Business In This State	<input checked="" type="checkbox"/> 4	<input checked="" type="checkbox"/> 4	Citizen of Another State	<input type="checkbox"/> 2	<input type="checkbox"/> 2	Incorporated and Principal Place of Business In Another State	<input type="checkbox"/> 5	<input type="checkbox"/> 5	Citizen or Subject of a Foreign Country	<input type="checkbox"/> 3	<input type="checkbox"/> 3	Foreign Nation	<input type="checkbox"/> 6	<input type="checkbox"/> 6
(For Diversity Cases Only)	PTF	DEF		PTF	DEF																				
Citizen of This State	<input type="checkbox"/> 1	<input type="checkbox"/> 1	Incorporated or Principal Place of Business In This State	<input checked="" type="checkbox"/> 4	<input checked="" type="checkbox"/> 4																				
Citizen of Another State	<input type="checkbox"/> 2	<input type="checkbox"/> 2	Incorporated and Principal Place of Business In Another State	<input type="checkbox"/> 5	<input type="checkbox"/> 5																				
Citizen or Subject of a Foreign Country	<input type="checkbox"/> 3	<input type="checkbox"/> 3	Foreign Nation	<input type="checkbox"/> 6	<input type="checkbox"/> 6																				

IV. NATURE OF SUIT (Place an "X" in One Box Only)					
CONTRACT	TORTS	FORFEITURE/PENALTY	BANKRUPTCY	OTHER STATUTES	
<input type="checkbox"/> 110 Insurance <input type="checkbox"/> 120 Marine <input type="checkbox"/> 130 Miller Act <input type="checkbox"/> 140 Negotiable Instrument <input type="checkbox"/> 150 Recovery of Overpayment & Enforcement of Judgment <input type="checkbox"/> 151 Medicare Act <input type="checkbox"/> 152 Recovery of Defaulted Student Loans (excl. Veterans) <input type="checkbox"/> 153 Recovery of Overpayment of Veteran's Benefits <input type="checkbox"/> 160 Stockholder's Suits <input type="checkbox"/> 190 Other Contract <input type="checkbox"/> 195 Contract Product Liability <input type="checkbox"/> 196 Franchise REAL PROPERTY <input type="checkbox"/> 210 Land Condemnation <input type="checkbox"/> 220 Foreclosure <input type="checkbox"/> 230 Rent Lease & Eject <input type="checkbox"/> 240 Torts to Land <input type="checkbox"/> 245 Tort Product Liability <input type="checkbox"/> 290 All Other Real Property	PERSONAL INJURY <input type="checkbox"/> 310 Airplane <input type="checkbox"/> 315 Airplane Product Liability <input type="checkbox"/> 320 Assault, Libel & Slander <input type="checkbox"/> 330 Federal Employers' Liability <input type="checkbox"/> 340 Marine <input type="checkbox"/> 345 Marine Product Liability <input type="checkbox"/> 350 Motor Vehicle <input type="checkbox"/> 355 Motor Vehicle Product Liability <input type="checkbox"/> 360 Other Personal Injury CIVIL RIGHTS <input type="checkbox"/> 441 Voting <input type="checkbox"/> 442 Employment <input type="checkbox"/> 443 Housing/Accommodations <input type="checkbox"/> 444 Welfare <input type="checkbox"/> 445 Amer. w/Disabilities - Employment <input type="checkbox"/> 446 Amer. w/Disabilities - Other <input type="checkbox"/> 440 Other Civil Rights	PERSONAL INJURY <input type="checkbox"/> 362 Personal Injury - Med. Malpractice <input type="checkbox"/> 365 Personal Injury - Product Liability <input type="checkbox"/> 368 Asbestos Personal Injury Product Liability PERSONAL PROPERTY <input type="checkbox"/> 370 Other Fraud <input type="checkbox"/> 371 Truth In Lending <input type="checkbox"/> 380 Other Personal Property Damage <input type="checkbox"/> 385 Property Damage Product Liability PRISONER PETITIONS <input type="checkbox"/> 510 Motions to Vacate Sentence <input type="checkbox"/> 530 General <input type="checkbox"/> 535 Death Penalty <input type="checkbox"/> 540 Mandamus & Other <input type="checkbox"/> 550 Civil Rights <input type="checkbox"/> 555 Prison Condition	<input type="checkbox"/> 610 Agriculture <input type="checkbox"/> 620 Other Food & Drug <input type="checkbox"/> 625 Drug Related Seizure of Property 21 USC 881 <input type="checkbox"/> 630 Liquor Laws <input type="checkbox"/> 640 R.R. & Truck <input type="checkbox"/> 650 Airline Regs <input type="checkbox"/> 660 Occupational Safety/Health <input type="checkbox"/> 690 Other LABOR <input type="checkbox"/> 710 Fair Labor Standards Act <input type="checkbox"/> 720 Labor/Mgmt. Relations <input type="checkbox"/> 730 Labor/Mgmt. Reporting & Disclosure Act <input type="checkbox"/> 740 Railway Labor Act <input type="checkbox"/> 790 Other Labor Litigation <input type="checkbox"/> 791 Empl Ret Inc Security Act	<input type="checkbox"/> 422 Appeal 28 USC 158 <input type="checkbox"/> 423 Withdrawal 28 USC 157 PROPERTY RIGHTS <input type="checkbox"/> 820 Copyrights <input checked="" type="checkbox"/> 830 Patent <input type="checkbox"/> 840 Trademark SOCIAL SECURITY <input type="checkbox"/> 861 HIA (1395ff) <input type="checkbox"/> 862 Black Lung (923) <input type="checkbox"/> 863 DIWC/DIWW (405(g)) <input type="checkbox"/> 864 SSID Title XVI <input type="checkbox"/> 865 RSI (405(g)) FEDERAL TAX SUITS <input type="checkbox"/> 870 Taxes (U.S. Plaintiff or Defendant) <input type="checkbox"/> 871 IRS - Third Party 26 USC 7609	<input type="checkbox"/> 400 State Reappointment <input type="checkbox"/> 410 Antitrust <input type="checkbox"/> 430 Banks and Banking <input type="checkbox"/> 450 Commerce <input type="checkbox"/> 460 Deportation <input type="checkbox"/> 470 Racketeer Influenced and Corrupt Organizations <input type="checkbox"/> 480 Consumer Credit <input type="checkbox"/> 490 Cable/Sat TV <input type="checkbox"/> 810 Selective Service <input type="checkbox"/> 850 Securities/Commodities/Exchange <input type="checkbox"/> 875 Customer Challenge 12 USC 3410 <input type="checkbox"/> 890 Other Statutory Actions <input type="checkbox"/> 891 Agricultural Acts <input type="checkbox"/> 892 Economic Stabilization Act <input type="checkbox"/> 893 Environmental Matters <input type="checkbox"/> 894 Energy Allocation Act <input type="checkbox"/> 895 Freedom of Information Act <input type="checkbox"/> 900 Appeal of Fee Determination Under Equal Access to Justice <input type="checkbox"/> 950 Constitutionality of State Statutes

V. ORIGIN (Place an "X" in One Box Only)						
<input checked="" type="checkbox"/> Original Proceeding	<input type="checkbox"/> 2 Removed from State Court	<input type="checkbox"/> 3 Remanded from Appellate Court	<input type="checkbox"/> 4 Reinstated or Reopened	<input type="checkbox"/> 5 Transferred from another district (specify)	<input type="checkbox"/> 6 Multidistrict Litigation	<input type="checkbox"/> 7 Appeal to District Judge from Magistrate Justice

VI. CAUSE OF ACTION	Cite the U.S. Civil Statute under which you are filing (Do not cite jurisdictional statutes unless diversity): <u>35 U.S.C. §146; 37 C.F.R. §31.303</u> Brief description of cause: <u>Action under patent laws for declaratory relief</u>
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VII. REQUESTED IN COMPLAINT	<input type="checkbox"/> CHECK IF THIS IS A CLASS ACTION UNDER F.R.C.P. 23 DEMAND \$ _____ CHECK YES only if demanded in complaint: JURY DEMAND: <input type="checkbox"/> Yes <input checked="" type="checkbox"/> No
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VIII. RELATED CASE(S) IF ANY	(See instructions): JUDGE <u>Joseph J. Farnan, Jr.</u> DOCKET NUMBER <u>06-00593-JJF</u>
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DATE <u>October 10, 2006</u>	SIGNATURE OF ATTORNEY OF RECORD
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FOR OFFICE USE ONLY RECEIPT # _____	AMOUNT _____	APPLYING IFP _____	JUDGE _____	MAG JUDGE _____
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AO FORM 85 RECEIPT (REV. 9/04)

United States District Court for the District of Delaware

Civil Action No. 06 - 629

ACKNOWLEDGMENT
OF RECEIPT FOR AO FORM 85

NOTICE OF AVAILABILITY OF A
UNITED STATES MAGISTRATE JUDGE
TO EXERCISE JURISDICTION

I HEREBY ACKNOWLEDGE RECEIPT OF 1 COPIES OF AO FORM 85.

10/10/06

(Date forms issued)

Matthew G. Marin

(Signature of Party or their Representative)

(Printed name of Party or their Representative)

Note: Completed receipt will be filed in the Civil Action